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ART. LXVIII.—OBSERVATIONS ON ACETATE OF ZINC.

By WILLIAM PROCTER, JR.

IN the last edition of the United States Pharmacopœia, the formula for preparing acetate of zinc was revised, the process by double decomposition between acetate of lead and sulphate of zinc was repudiated, and a new method adopted, which consists in precipitating the lead from a solution of acetate of lead, by introducing into it a quantity of metallic zinc. When the materials employed are pure, the salt can be obtained by this process with the utmost readiness, and in a beautifully crystallized form; but if, as is often the case, the zinc employed contains iron, the salt is always contaminated with the acetate of that metal, which gives it a yellowish brown colour. The solution of acetate of zinc when first separated from the metal is colourless, the iron in it being in the state of protoxide, but by standing exposed to the air, or by heat, it gradually assumes the form of sesquioxide, and communicates colour to the solution.

It is with a view to this condition that the Pharmacopœia directs the addition of a filtered solution of chlorinated lime; the lime of the added salt displacing the ferruginous oxide, which is at once peroxidized by the action of the chlorine. This operation succeeds best when the iron is in its first,

stage of oxidation, or else it will seldom answer the end in view, and frequently fails altogether.

The author on a recent occasion in preparing several pounds of this salt, employed an article of zinc, said to be free from iron, but which was found to have contained a considerable portion of it. In resorting to the calcareous chloride for assistance in the difficulty, it was found that repeated additions of the chloride failed to separate the iron, the solution became amber-coloured and transparent.

In seeking for a remedy, a trial was made by boiling the coloured solution with hydrated carbonate of zinc and filtering, which was found to separate the iron entirely, affording a perfectly pure and colourless solution of the acetate. The best plan of proceeding is as follows: Separate about one-thirtieth part of the colored liquid, add a slight excess of carbonate of potassa and wash the resulting carbonate of zinc until freed from acetate of potassa. The magma of carbonate of zinc thus obtained is added to the boiling solution in divided portions, until, on filtering a little of the liquid, it is found colourless; when the whole should be filtered off from the colored carbonate of zinc, evaporated and crystallized.

Since employing the above method, a more simple, though less unobjectionable application of the same principle has been tried, which consists in merely throwing into the coloured acetate a solution of carbonate of potassa; of course carbonate of zinc and acetate of potassa are produced, and the carbonate, from being presented in its nascent state, is peculiarly fitted for acting on the acetate of iron. The small quantity of acetate of potassa in the solution remains in the last mother liquor.

This method of using the hydrated carbonate of a metallic oxide to free its soluble salts from iron, has been employed in the case of manganese; but I am not aware of its having been used with this intent in the case under consideration.

Whilst on this subject it may be well to make a few remarks touching other points in the manufacture of this salt, for the benefit of those who may not have learned them by experience.

1st. The large amount of zinc directed in the Pharmacopœia is not necessary when the metal has a great surface in proportion to its weight; as when in the form of sheet zinc. 2d. It sometimes happens that the precipitation of the lead proceeds very slowly, which is owing to the surface of the zinc being coated with oxide or other foreign matter. By washing the zinc with diluted acetic acid, before introducing it into the solution, it acts very promptly. 3d. As in large operations it is of much importance to employ as little fluid as the nature of the case will admit, in order to save evaporation, it has been found that by mixing the sugar of lead with one-half of the prescribed quantity of water, the excess of it is gradually dissolved and decomposed as the operation proceeds, because the resulting acetate of zinc is less bulky and more soluble than the lead salt. 4th. In effecting the crystallization of acetate of zinc, it frequently happens that instead of brilliant six-sided plates or tables of large size, the salt is deposited in minute scales or crystals, radiating from centres which form a thick magma with the mother liquid, difficult to drain. This is owing to concentrating the solution too much, or to cooling it too rapidly, or both. By adopting Faraday's suggestion of removing a drop to a glass plate from time to time, as the evaporation proceeds, the proper point of concentration is easily ascertained. Sometimes, however, this imperfect crystallization is owing to the presence of a less soluble sub-salt, (caused by the loss of acetic acid) which is known by the opacity of the liquid when an attempt is made to re-dissolve the acetate. In order to remedy this it is necessary to add as much acetic acid to the hot concentrated solution before crystallization, as will enable that solution to retain its transparency when added to twice its bulk of water.

ART. LXIX—AN ADDRESS DELIVERED TO THE GRADUATES OF THE NEW YORK COLLEGE OF PHARMACY, NOV. 20th, 1845. By GEORGE D. COGGESHALL, Esq., Vice President of the College.

At a stated meeting of the College of Pharmacy of New York, held November 20th, 1845, Messrs. Buckland W. Bull, Joseph Roberts, and William B. Riker, were declared graduates in Pharmacy; whereupon they were addressed by George D. Coggeshall, Esq., one of the Vice Presidents of the College.

On motion, the Secretary was requested to call on Mr. Coggeshall, and request a copy of his address for publication in the American Journal of Pharmacy.

JOHN MEAKIM, Secretary.

ADDRESS.

GENTLEMEN, GRADUATES OF THE COLLEGE:

It has become a part of the business of this meeting to confer upon you a testimony of honor and confidence to which you have earned a title by diligence in practical and theoretical study. We trust that while it may prove to you a letter of credit, wherever your future course may be directed, it will ever be an incentive to honor the institution which has cherished you, as you best can do, by faithfully and zealously performing the duties of your profession.

And we would earnestly press upon your attention that your studies, though with good conduct, they have brought you to an auspicious point, have but fairly commenced. The field of learning which opens before you, is too vast to be embraced in the teaching of any school, in which the main outlines and points of every day concern only can be enforced, giving the student, however, a direction and onward impulse, very helpful to him certainly, but which he

must energetically maintain for himself. Unfortunately, too, the schools of Pharmacy in our country, are feeble in resources, unaided by government, and as yet, except in a limited degree, by public opinion. They were originated, and have been sustained, thus far, by the resolute and unselfish labors of men engaged in business, who had least to gain by their successful prosecution, aided in progress of time by their own graduates, who, from industrious students, have come to rank among their most esteemed and efficient co-laborers.

Institutions devoted exclusively to the advancement of our art, have long flourished in Europe, deriving patronage and power from their governments, possessed of most extensive libraries, cabinets and variety of apparatus for chemical and philosophical demonstrations. In these schools the teaching of Pharmacy and its collateral branches of science, extending beyond our courses to Botany, Mineralogy, Geology, Natural Philosophy, Physiology, Toxicology, and Medical Jurisprudence, has attained a degree of excellence which we can scarcely hope to reach until the general sentiment shall demand it. There, too, learners of our business are required to possess previous qualifications, are subjected to a length of laborious servitude, followed by searching, minute and extended examination; and those who practice it, though protected in their rights and privileges, are held to a rigorous accountability, which in the individual latitude enjoyed—or rather suffered—under our laws, could hardly be realized, and if they existed, would deter many from encountering their difficulties.

Yet if we have approached so distantly the standard of schools in older nations, we may congratulate ourselves on having done much according to our ability. The improvement in the appearance of our stores, in the degree of cleanliness, and method of their manipulations, in the number and accuracy of their preparations, and more than these, in the

quality of drugs and chemicals which they dispense, are abundantly manifest to all whose duties or necessities make them acquainted with the subject. Our meetings have been pleasant occasions for mutually extending information on all matters concerning our business. An increasing spirit of emulation has also been excited in our students, prompting them to obtain their degrees with something more of credit than mere form, and this promises well for the future. We regret that we have been unable to do more for them; we hope they will help us to do more for their successors.

Gentlemen, you are about to enter upon the discharge of duties, the importance and responsibility of which, are most felt by the most virtuous minds. Upon the Apothecary, of all men, the Golden Rule is laid with most emphasis. With whatever anxious care you select, with whatever watchful precision you weigh, measure, and combine for yourselves or for any one whom you hold in more regard than yourselves—"you should do even so unto others." Those who repose their trust in you may have equally vital hopes and interests in jeopardy, which must not be sacrificed by the slightest failure in any part of your duty. Strive to emulate the achievements and fame of men, who from humble origin have taken rank amongst the greatest benefactors of mankind, and have shed lustre over our profession. But if you do not reach their eminence—if it should not be your supreme good fortune to light a safety lamp, or to demonstrate the existence of proximate principles—"all stars cannot be of the first magnitude"—you may yet, if you will, occupy the station which is your lot with great practical usefulness to all around you. Let incorruptible integrity be your chief governing principle. Upon such a basis you cannot but found an honorable character, for you will be impelled to the best exertion of all your faculties. Let no prospect of gain ever tempt your manhood from a straightforward honest course, down into the infamous arts of quackery. Your legitimate business, honestly and indus-

triously pursued, will scarcely fail to give you competence, will certainly ensure you a peculiar and a higher degree of respect than is shown to general tradesmen, and above all—though it may not be fully appreciated on “Change”—the countless treasure of a good conscience.

The College of Pharmacy of the City of New York, upon the recommendation of its Board of Trustees, declares Buckland W. Bull, Joseph Roberts, and William B. Riker to be Graduates in Pharmacy, and awards to each of them its Diploma.

ART. LXX.—REMARKS ON THE PREPARATIONS OF SENEKA.

By WILLIAM PROCTER, JR.

HOWEVER useful the properties of a drug may be in a medical point of view, it depends often in great measure on the skilful application of the Pharmaceutic art, whether the physician derives that degree of assistance from its use which he anticipates, and of right expects. Among the valuable remedies composing our indigenous *Materia Medica*, perhaps no one has acquired more celebrity than Senega, and it is with the design of attracting the attention of pharmacutists to the preparations of this drug, that the following remarks are made.

Five successive analyses by Gehlen, Feneulle, Dulong, Folchi, and Quevenne, have thrown much light on the proximate chemical constitution of the root of *Polygala senega*, but it is more especially to the latter chemist that we are indebted for this knowledge. In the 22d volume of the *Journal de Pharmacie*, M. Quevenne has published an elaborate essay on this

subject, comprising a history of its constituents, and particularly of its active principle, *polygalic acid*, which he describes as a white, inodorous, pulverulent substance, unalterable in the air, and capable of producing very energetic effects on the animal economy. Its acid character appears to be well established, as it reddens litmus and combines with bases to form salts, which are uncrystallizable, but its intensity is so slight that it is incapable of displacing carbonic and hydrosulphuric acids from their combinations. It is this principle which causes the decoction of seneka to redden litmus, and which gives it the tendency to froth by agitation. It is analogous in many of its properties to saponin, and in some respects to sarsaparillin. When in a pulverulent form it is brought in contact with the nasal membrane, it produces sneezing and local inflammation of the part, and when swallowed causes a painful astringent sensation in the throat.

Polygalic acid in a free state dissolves but slowly in cold water, but with great readiness when assisted by heat; nevertheless cold water removes it completely from the powdered root, which may be due to its association with other principles, as in the cases of sarsaparillin, cantharidin, etc. Boiling alcohol dissolves it largely, from which by cooling it precipitates in a pulverulent form, and this is true also of dilute alcohol. Perhaps those who have prepared a tincture of seneka with the intention of resorting to it as occasion might require for making the syrup, have noticed a light coloured precipitate to separate after standing some time. This is polygalic acid, and should not be removed, as it will redissolve by the heat requisite in the evaporation of the alcohol. This principle, notwithstanding its acid nature, appears to be incompatible with but few substances, and according to M. Quevenne, it may be associated without impropriety with all ordinary salts, except subacetate of lead and protonitrate of mercury. M. Quevenne isolated polygalic acid by treating the root with cold water by displacement, precipitating the cold infusion with

subacetate of lead, washing the precipitate with water, suspending it in that fluid, and the lead precipitating by a current of sulphuretted hydrogen. The filtered liquid is then evaporated to an extract, this exhausted by boiling alcohol 40° Baumé, and the extract resulting from the evaporation of this alcoholic fluid treated with water, which takes up the polygalic acid and leaves a yellow matter. The solution containing the polygalic acid is again treated with subacetate of lead, sulphuretted hydrogen and evaporation, and the extract obtained is dissolved in boiling strong alcohol which deposits the polygalic acid in a pure state by cooling.

Polygalic acid may be obtained pure enough for medical use, by treating the powdered seneka with boiling alcohol of 35° Baumé until exhausted, removing the alcohol by distillation until the fluid is reduced to a syrupy consistence, then treating it with ether to remove fatty and resinous matter, and mixing with a quantity of cold strong alcohol—which, by standing several days, precipitates the acid of a light brownish colour. In this state it is impure, and requires to be redissolved in hot alcohol boiled with animal charcoal and filtered while hot. When it separates in a pulverulent form, M. Quevenne has proposed the employment of polygalic acid as a therapeutic agent and from its easy preparation and great activity, there appears no good reason why it should not be added to the list of medicinal proximate principles. The physician would be enabled to control the action of the remedy more completely, and by combining it with other substances, to modify its influence. The patient would be less inconvenienced by its administration, as its concentrated form admits of its being more easily disguised in mucilage in syrup or in pill.

From an approximative estimate, M. Quevenne infers that one grain of polygalic acid represents the activity of a dram of seneka.

The following formula would represent an ounce of the root and a pint of decoction, or four fluid ounces of the syrup :

Take of Polygalic acid	-	-	-	grs. viij.
“ Boiling water	-	-	-	f. ʒss.
“ Syrup of gum arabic	-	-	-	f. ʒiiss.

Dissolve the acid in the warm water and add the gum syrup; one fluid-dram of this syrup would be equivalent to half a dram of seneka. The addition of ten drops of liquor potassæ will supercede the necessity of the water being hot, as the alkaline polygalate is very soluble—while at the same time its activity is not decreased.

The officinal preparation of seneka, which has received the most universal employment, is the decoction. It is the only one to be found in the British Pharmacopœias, and this may be looked upon as an evidence of the low esteem in which seneka is held by the practitioners of Great Britain, a fact admitted by Pereira. It is but seldom that the apothecary is called upon to prepare this decoction, the physician directing a quantity of the root, often in combination with some other remedies, to be placed at the disposal of his patient, with directions to pour a certain quantity of water on it, and boil for a given time, or until reduced to a stated measure.

From imperfect manipulation, assisted, perhaps, by the want of a proper degree of comminution, the root is but half exhausted. It has frequently happened, owing to the omission of directions in the prescription, that the unbroken roots have been used to make the decoction!

In every case where such substances are prescribed with a view to their being prepared by the patient, the pharmacist is justified in assuming the interpretation of the prescription by reducing them to a proper state of division.

When prepared by the apothecary, if time is allowed, resort should be had to the method of displacement which yields a transparent and more concentrated infusion; but if that is inadmissible from limited time, or the nature of associated substances, maceration in warm water, (120° Fahr.) and subsequent expression, will be more appropriate. It is best to associate with the decoction some demulcent substance to mask

its acrimony. The Hamburg Pharmacopœia directs Iceland moss, liquorice is often used, and slippery elm, and flaxseed are occasionally prescribed.

In the 15th volume of this Journal, the writer offered a formula for the preparation of an extract of seneka, which consisted in exhausting the root with diluted alcohol and evaporating the tincture carefully to the consistence of an extract; and proposed its employment in medicine, both in pill and as a ready means of making the decoction. This extract dissolves almost entirely in water, and affords a more eligible preparation than that by the officinal formula; and by its means the preparation can be dispensed at once. It may be as well to observe that the displacement of seneka is effected with greater rapidity by employing a menstruum composed of two parts of water and one of alcohol; the maceration may be continued longer in warm weather without fear of change, and is more readily evaporated.

The syrup of seneka when properly prepared is a very efficient preparation, one pint embodying the strength of four ounces of the root. The framers of the United States Pharmacopœia in adopting the method of displacement as a means of exhausting the activity of medicinal substances, have almost invariably given the old formula, at the same time, as a cautionary measure, founded on the presumed want of knowledge on the part of the apothecaries of this country, of the proper application of that principle. This, as a progressive movement, was doubtless a wise precaution, but it is to be hoped that the experience which shall have been acquired in its employment by the next revision of that work will justify the unconditional adoption of that useful process in every case where it is proper, and its rejection otherwise.

The syrup prepared by the second formula of the Pharmacopœia is in all respects preferable to that by the first, or boiling process. The latter directs four ounces of bruised seneka to be boiled in a pint of water until the menstruum is reduced

one half, then strained, and afterwards made into a syrup with the sugar. If these directions are literally followed, a syrup will be obtained super-saturated with sugar, because when it is attempted to strain a concentrated decoction of seneka composed of eight fluid ounces of liquid, with four ounces of seneka, in its swelled state, disseminated through it, not more than four or five fluid ounces will be obtained, unless subjected to much greater pressure than is at the command of most apothecaries, and consequently, unless in case the fluid is made up by the subsequent addition of water, the syrup contains too much sugar, and in either case will not embody all the strength of the root employed. A better plan would be to infuse the root in a close vessel until it was exhausted, then strain the infusion, and by subsequent evaporation reduce it to the required measure. The formula for compound syrup of squill (which would be more correctly designated compound syrup of seneka) has been amply discussed in a preceding volume of this Journal.

ART. LXXI.—PROCESS FOR PREPARING VALERIANIC ACID.

BY MESSRS. T. AND H. SMITH.

HAVING of late had considerable demand for valerianate of zinc, in consequence, probably, of a desire among medical men to test its value as a therapeutic agent, we were led to inquire whether a method of obtaining the acid of valerian more quickly and abundantly than by the usual process, so very unsatisfactory in these respects, could not be devised. The method we adopted completely answered our expectations, and as it may be of some use as a guide

to other chemists, who may have occasion to prepare valerianic acid, the process is subjoined.

Let the valerian be boiled for three or four hours in rather more than its bulk of water, holding in solution an ounce of carbonate of soda for every pound of the root, and replacing the water as it evaporates. Let the liquid be strongly pressed out, and the residuum again boiled for a little with a like quantity of water. After another pressing, let the process be repeated in the same way, a third and last time. After mixing the liquids, and adding two fluid drachms of strong sulphuric acid for each pound of the root used, let them be distilled. When about three-fourths of the liquid have passed into the receiver, let the distillate be fully neutralized with carbonate of soda, for which purpose a quarter of an ounce for every pound of the root will be quite enough. The valerianic acid can then be obtained in the usual way—viz., by concentrating the solution of valerinate of soda, decomposing it with sulphuric acid, and separating the valerianic acid, now set free, either by means of a separator or distillation. When the valerianic acid has been once obtained, no difficulty can occur in preparing any of the valerianates.

The advantage of this method over that in which the root itself is simply distilled with water, will be seen on contrasting the results of both. By the latter method, the time required was six times greater than when the valerinate of soda in solution was distilled after adding a strong acid; and although the sacrifice of time was so much greater in the first case, the contents of the still continued to smell strongly of valerian, while in the latter, not a trace of the peculiar odor of valerianic acid could be detected, showing that the principle had been more effectually exhausted. And further, the amount of acid obtained, four scruples from the pound of root, was nearly thrice as great as could be got without the use of soda.

Since the above process was adopted by us, M. S. Ra-

bourdin, Pharmacien à Orléans, has published in the *Journal de Pharmacie*, a method suggested apparently by views of the subject similar to our own. He conceived that the valerianic acid might be partly in combination with a base, and that, by adding a strong acid, the volatile acid would be completely set free, so that, on distillation, a much larger product would be obtained. The result wholly justified his preconceptions. Five kilogrammes of the root gave from forty-five to fifty grammes of the acid, a result closely agreeing with the quantity produced by our own process.

The principle of the process suggested is very simple. In the one case an acid is presented to a valerianate, or supposed valerianate, to free it from combination with its base, by the exertion of a stronger affinity; while, in the other case, a base (soda) is presented to the valerianic acid, powerful enough to cause its effectual separation from that with which it was previously combined.

The two processes serve the same end; but it seems to us that the latter is, on the whole, to be preferred, principally because it has the advantage of presenting the acid in a state of complete solution, from which the operator can get it more easily and effectually detached, than when contained in the hard unyielding cells of the woody fibre.—

Chemist, from London Lancet.

ART. LXXII.—ON THE TRANSFORMATION OF PERCHLORIDE OF MERCURY INTO PROTOCHLORIDE, BY CERTAIN PHARMACEUTICAL PREPARATIONS. COMPOUND PREPARATIONS OF MERCURY NOT INCOMPATIBLE WITH THESE PREPARATIONS.

By M. LEPAGE.

MORE than forty years since M. Boullay, at the present day one of the most learned professors of French pharmacy, pointed out the reduction of perchloride of mercury (corrosive sublimate) by contact with the syrup used in cookery, and its transformation under these circumstances into protochloride or calomel.

The observations of M. Boullay have, since the time he made them public, been confirmed by many experimentalists. Very recently, also, a distinguished chemist, M. Mialhe, read a paper before the *Société de Pharmacie*, on several experiments of his own, during which he also recognized the transformation of sublimate into calomel by mixture with several pharmaceutical preparations, and particularly with the cook's syrup, a phenomenon this chemist attributes to the *glucose* the preparation contains.

M. Mialhe has also discovered that the perchloride of mercury remains unaltered by the contact of pure syrup of sugar. Having had occasion to devote ourselves for some time past to experiments on the same subject, we, also, believe it to be our duty to inform the *Société de Pharmacie* of the results. Our experiments teach us:—

1. That corrosive sublimate placed in contact with the cook's syrup, is completely decomposed and converted into calomel. The transformation begins immediately the mercurial salt and syrup are mixed, and it is first perceived by the syrup losing its transparency. As fast as the calomel is generated it falls

by little and little, to the bottom of the vessel, and after some time it may be collected to be subjected to particular examination.

2. That sal-ammoniac, and other alkaline chlorides, do not prevent the change taking place, and that, in as short a space of time, contrary to the opinions of some writers, who pretend, that in such a case, in the instance of sal-ammoniac, for example, when added to the mercurial salt, it gives stability to it, and prevents the reduction taking place.

3. That with the cook's syrup, previously acidulated by a few drops of hydrochloric acid, the reduction of the sublimate into calomel, equally takes place.

4. That the simple syrup of sarsaparilla (prepared from the hydro-alcoholic extract of the root, according to the formula) also transforms the sublimate into calomel.

5. That the syrup of honey, completely freed from the wax by means of chalk, also effects its reduction; but that with this and the preceding preparation, the complete transformation appears to be much slower in being effected, for we have found it possible, after a contact of two months, to separate a small quantity of sublimate by shaking it up with ether, while we have been unable to discover that salt when mixed with the cook's syrup, after the same lapse of time, and by resorting to the same means.

6. That the pure syrup of sugar does not decompose the sublimate, as M. Mialhe has also ascertained.

In the presence of there being well-established facts of which a good many medical men hold no account, for we still see them, we may almost say, daily prescribe sublimate mixed with cook's syrup, or some analogous preparation, we have asked ourselves if, among the soluble preparations of mercury possessing medicinal properties analogous to those of sublimate, there may not be some which could be mixed with syrups loaded with extractive matter, without undergoing decomposition? We have made experiments on this subject, and have

discovered that bicianuret of mercury* and the iodhydrargyrate of ioduret of potassium, which, as it is known, possesses properties very analagous to those of perchloride of mercury, are not affected by the above mentioned preparations, which transform sublimate into calomel. We possess mixtures of these two substances, with the cook's syrup, made more than a year back, in which the cyanurate and the iodhydrargyrate have experienced no decomposition.

The iodhydrargyrate of the ioduret of potassium, discovered by the late Polydore Boullay, has been, as we know, frequently employed with success, for several years, by Dr. Puch, physician to the *Hôpital du Midi*, as a remedy in syphilitic diseases. It is usually prepared by combining equal parts of ioduret of mercury and ioduret of potassium.

We entreat those physicians who, for the future, wish to combine a vegetable with a mercurial treatment, to consider the facts we have here related.—*Chem. from Jour. de Pharm*

ART. LXXIII.—ON AQUA REGIA; ON HYPONITRIC ACID, AS A MEANS OF OXIDATION; ON THE CONSTITUTION OF THE SAME ACID, AND THE PART IT ACTS ON BEING PUT IN CONTACT WITH ORGANIC SUBSTANCES.

By DR. KENE, Professor of Chemistry at Brussels.

Continued from p. 211.

On the part which Hyponitric Acid acts when in contact with Organic Substances.

22. THE property of hyponitric acid to convert most bodies into oxides of the highest stage of oxidation, is attri-

* The basic cyanuret of mercury (oxycyanuret,) however, deposits after a time almost inappreciable traces of metallic mercury, by contact with the cook's syrup.

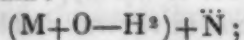
butable to its sparing degree of stableness. This property is one of the causes owing to which the acid in question is devoid of the principal character of acids. It has, therefore, no other function than that of oxidating; as it cannot combine with chlorine, whatever be the circumstances under which these two bodies are brought together; be it in a nascent state in the presence or absence of water, at a moderate or low temperature, and even in the presence of a powerful base,* chlorine will invariably be disengaged as soon as the hydrogen of the hydrochloric acid begins to act on the oxygen of the nitric acid (19). Of this body, no other combination with an elementary substance is known than that with oxygen; and it may be anticipated, that it will never be possible to form any, as this cannot be brought about with chlorine, which, owing to its great analogy with oxygen, relative to polarity, is able to act a part analogous to that of the said metalloïd.

The hyponitric acid, therefore, does not act in the manner of compound radicals. May it be supposed that in some organic combinations it acts the part of a single body? In the present state of science, this is a question of the highest importance; and it may even be anticipated, that the future state of the chemistry of compound radicals will depend upon the precision with which this question will be settled.

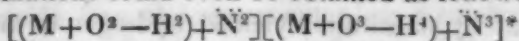
23. By reacting upon an organic substance, and by oxidating one equivalent of hydrogen, according to the principles of the theory of substitution, nitric acid forms ($M-H^2 + \ddot{N}$.) it appearing, from the analysis of the fresh combination, that M by losing H^2 has combined with $N^2 O^4$.

* We satisfy the latter condition by directing a current of hydrochloric acid into nitre. If the salt is quite dry, at a common temperature, no action takes place; on applying, however, a gentle heat, or on making use of nitre which is not dry, chlorine, water, and nitrous vapors, are formed, products resulting from the influence of the water on the vapors; and, finally, chloride of potassium is left behind.

According to Berzelius, however, the new combination has to receive the formula :



and combinations could even be obtained as follows :—



Hence, according to the first hypothesis, the fresh combination is corresponding with that on which the nitric acid acted ; whereas, according to the second, it is composed of nitrous acid and an oxide of a compound radical.

We have, therefore, in the above instances two hypotheses, leading to different theoretical views, as they emanate from an arrangement of combinations, which is not one and the same in both. Investigations calculated to support one or the other of these hypotheses are highly important in the present state of science, and the more so as the establishing of one of them will be the means of ascertaining the constitution of organic combinations, and thus raise the study of these combinations to the rank of an accurate science.

24. *That the hyponitric acid in organic bodies does not act the part of a radical, appears from the foregoing experiments and considerations, especially from the action of hydrochloric acid on nitrate of potassa.*

Previous to having established this fact, I gave credit to the hypothesis of MM. Dumas and Couërbe. What resulted from other experiments relative to the nature of oxysulpho-sulphuric acid, did not remain without influence on my views of that of hyponitric acid. Not knowing, however, which is the precise part acted on by this acid, and considering it as a dehydrogenating body kindred to chlorine, I was of course induced to consider this as a radical, as is done with the latter metalloïd, which in organic substances

* As it is impossible to enter now into the details of the above two hypotheses, we leave unmentioned the circumstances under which the said process appears to others, when nitrogen or nitrous oxide enters into the compound radical. Our object was merely to bring into a parallel the principles of the views relating to the matter.

may frequently displace the hydrogen. It is owing to the dehydrogenating power of the hyponitric acid, that its elements have been found in several combinations formed by its influence, in the manner of chlorine, which is found in a body, that by substitution yielded hydrogen to that metalloid.

Though the hyponitric acid, however, in the presence of several organic bodies may act in the manner of chlorine, it is yet not proved, that it really acts like the said metalloid, under circumstances in which it behaves like a simple body. The hypothesis of the function of this acid, therefore, reposing only on theoretical observations, and not being warranted by a single well-established fact, it became necessary to base it on rigorously examined facts. It having, however, appeared, from our investigations, that the hyponitric acid does not act the part of a radical, not even with reference to the body, which, relative to polarity, offers the greatest analogy with oxygen, we attempted to explain the action of this acid on organic bodies in another manner, considering it as a means simultaneously oxidizing and dehydrogenating. Free, therefore, from any preconceived opinion, we have examined Berzelius's theory, which we have found to agree with the present state of science, and to explain most of the facts ascertained in a satisfactory manner, to such an extent that, with some restrictions, we do not hesitate to give it our sanction.

25. *That the hyponitric acid, relative to organic bodies, acts the part of an oxidating and dehydrogenating means, is a conclusion directly to be deduced from its oxidating power, as an organic body, by being transformed, yields a combination, which is the more stable the more complete the change is. The hyponitric acid, if it partially dehydrogenates a body, or if it forms a combination, on which, under the circumstances then taking place, it no more exerts any dehydrogenating influence; it may convert this*

body into an oxide, an acid, and sometimes even into a salt.

26. The oxide, at the moment of its formation, may combine with nitrous acid, the oxidating power of which is less than that of the two other acids of nitrogen.*

If the oxide formed does not enter into a combination, it continues to remain under the influence of the oxidating agent, it is raised to higher stage of oxidation, and converted not either into a simple nitrogenous acid (effect of nitric or hyponitric acid on ethereal oils, on paraffin, &c., substances free from oxygen,) or into a nitrogenous double acid (nitro-naphthalinic acid, &c.)

If, finally, this acid reacts on an oxysalt, produced by its influence, a salt may be formed raised to a higher stage of oxidation (effect of nitric acid on naphthalin, benzin, &c.)

Even by other acids than those formed by the influence of the said acids, the oxidation may be brought about (effect of hyponitric acid on neutral fatty bodies.)

The formation of organic, not nitrogenous, acids, produced under circumstances as above, and the effect of hyponitric acid on fatty matters, are most important facts, serving as evidence that this acid acts, indeed, the part of an oxidating as well as of a dehydrogenating means.

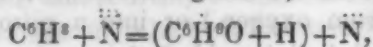
If, however, an oxyacid, with compound radical, containing hydrogen, may be produced by the oxidating action of hyponitric acid, it may, likewise, happen, that by the action of the same, or of that of nitric acid, on other organic bodies bases may be formed, acidity and basicity being respectively dependent on an opposed tendency, resulting from the various manners in which the molecules are arranged, or the circumstances under which this grouping takes place, and on those under which these bodies combine, &c. Nothing, therefore, stands in the way of the for-

* From instances to be adduced in the sequel, it will appear that these processes are, indeed, of the kind as stated.

mation of a base, which combining with the least powerful oxidating means, resulting from the partial deoxidation of the nitric and hyponitric acids, it yields a nitric salt.

27. On allowing concentrated nitric acid to act, for instance, on acetone $C^5H^{12}O^2$, two combinations are obtained $(C^6H^6O + \ddot{N})$, $(C^6H^6 + \ddot{H})$ which result from the dehydrogenating action of this acid; the elements of the base C^6H^6O , in this case, are present in the acetone.

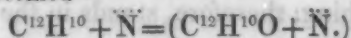
If, however, this acid is allowed to act on mesitylen, it likewise produces an oxidating effect; there results,



because the radical C^6H^6 requires oxygen to form a base. That the reaction takes place in the manner indicated by the above equation is proved by the fact, that the chlorine forms with the same substance a base corresponding to nitrate of oxide of pteylel, acting simultaneously as a dehydrogenating and chloridising means.

Owing to the existence of the radical pteylel forming an oxide with oxygen, which sometimes combines with nitric acid, and on other occasions with water, chlorine, and nitric acid with mesitylen yield combinations, which bear no parallel, though the reaction of these agents is in fact one and the same; this, however, is merely meant according to the hypothesis of Berzelius, as, according to that by which the hyponitric acid is considered as a radical, we cannot account for this fact, since the nitric acid, by reacting on the mesitylen, gives no combination, into which the hyponitric acid enters as a constituent; hence it does not yield a combination constituted in a manner analogous to that of the product resulting from the reaction of chlorine or mesitylen.

28. If water be added to a hot solution of benzin in nitrous acid, it will be formed—

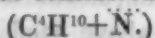


That this fresh combination is not a corresponding one to $(C^{12}H^{10} + \ddot{S})$, but a salt formed by the combination of the pro-

toxide of benzin with nitric acid, appears from the fact, that when the solution of this salt in the nitrous acid is allowed to boil, the protoxide of benzin is converted into the oxide of benzin, and the salt ($C^{12}H^{10}O^2 + 2\ddot{N}$) is formed.

29. Toluin, by being treated with boiling nitrous acid, likewise forms nitrite of oxide of toluin; whereas the nitrite of protoxide of toluin is formed, if the above treatment takes place at the common temperature (Deville.)

30. If naphthalin is allowed to boil with nitric acid until the oil formed on the surface of the liquid ceases to exhibit the properties of naphthalin, according to Laurent, the combination ($C^{20}H^{14} + \ddot{N}$) is obtained. To this Berzelius objects, that if the said combination would be thus constituted, the nitrite of oxide of ethyl ought to be considered as consisting of



To this I add, that under similar circumstances the paranaphthalin yields a combination free from nitrogen, and that if the action of the nitric acid be somewhat longer continued, the nitronaphthalese would be converted into nitrite of oxide of naphthyl $2(C^{10}H^7 + \ddot{N}) = C^{20}H^{14}O^2 + 2\ddot{N}.$ * In the same manner as nitrite of the protoxide of benzin or toluin, under similar circumstances are respectively converted into the oxides of benzin and toluin. The nitronaphthalese ($C^{20}H^{14}O + \ddot{N}$) and the nitronaphthalese ($C^{20}H^{14}O^2 + 2\ddot{N}$) are, therefore, saline combinations, which may be respectively called the nitrites of protoxide and of oxide of naphthyl, designating, by the term naphthyl the radical, $C^{20}H^{14}$ of naphthalin.

31. It appears from the above instances, that by the combined influence of the application of heat, and the action of either the nitric or the hyponitric acids, an oxide of a radical may be raised to a higher stage of oxidation. This radical,

* From the analysis of this combination resulted 2.90 of hydrogen. According to calculation it ought to have been only 2.41, supposing in the combination to be present six atoms of hydrogen for ten atoms of carbon. But $2.41 : 2.90 :: 6 : 772$, it follows that the empirical formula is not $C^{10}H_6N^2O$, but $2C^{10}H^7N^2O = C^{20}H^{14}N^4O^2$.

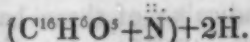
however, being formed, by the influence of a dehydrogenating action of these acids, the oxide produced by the oxidating action of the same agents, it may easily be conceived, that if the reaction is longer continued, or made to work more energetically, the radical may simultaneously be changed, and oxides formed, containing a larger amount of oxygen than those previously produced. M. Laurent has, indeed, observed, that if the acid solution of the nitrite of oxide of naphthyl is allowed to boil until an oily body separates, a combination is formed, which the French chemist designates by the name of nitro-naphthaleïse, which, however, is more properly called nitrite of oxide of naphthaleïn (azolite naphthaleïsique) considering the formula ($C^{40}H^{24}O^5 + 5\ddot{N}$) which probably expresses its combination. If naphthalin, and nitric acid are boiled together, for four or five days, the above combination is converted into nitronaphthalese, or into the combination ($C^{20}H^{10}O^3 + 3\ddot{N}$), which in the manner of that just quoted contains as many equivalents of acid as are equivalents of oxygen contained in the base. The fresh salt, therefore, is the nitrite of oxide of naphthalin.

The combinations in question, instead of being composed of an oxybase and nitric acid, contain, as the electro-negative constituent that of the three oxyacids of nitrogen, which is the least endowed with the power of oxidating, an energetically oxidating body being unable to expel the nitrous acid from its combination without changing the radical of the base.*

After this change, however, has once taken place, the nitric acid acts more intensely; the fresh radical is invariably more stable than the foregoing one (25,) it may form with oxygen a more stable base, and the oxide thus produced may combine

* It is with these salts, as with the compound kinds of ether, they cannot be brought under the law of Berthollet, because the nitric acid employed to expel the nitrous acid from its combinations, must act with an energy calculated to decompose the radical either wholly or partially. The discovery of the cause of this anomaly is indisputably one of the most important which in organic chemistry ever could have been made.

with a more energetic acid, even if the latter body be of the most powerful oxidating agents. In this manner, owing to a material change, by nitric acid, two acids are produced from *indigo*, in which the presence of nitric acid seems probable, and by a change similar to that which naphthalin undergoes when treated with this acid, a double acid is formed—

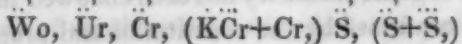


It is owing to the same cause that, by the direct action of nitric acid on wood spirit, the oxide of methyl, without being altered, may combine with this acid, whereas the base of alcohol, being less stable, reduces the nitrous acid to the stage of a less powerful oxidating agent to that of nitrous acid (21,) which may combine with another portion of the oxide of ethyl, that which has not been destroyed.

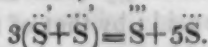
33. We have hitherto met with no difficulties regarding the explanation of the phenomena generally perceived by the reaction of either nitric or hyponitric acid on organic bodies. The reason of this is, that we admitted as correct Berzelius's hypothesis, according to which the organic combinations containing oxygen, consist of the latter metalloïd, and a radical. This hypothesis, however, is far from being opposed to facts, with which organic chemistry has been endowed in latter days; it is rather confirmed by the constitution and properties of the products formed by the action of several oxidising agents on a great number of hydro-carbonaceous substances; by the constitution of ethereal combinations, and others analogous to the latter; by the various stages of oxidation of acethyl, formyl, &c.; by the circumstances under which the artificial valerianic acid is formed; by the analogy of the constitution of margarylic or hypo-margarylic acid; by that of the proteïn, and of the two higher stages of oxidation, serving to regenerate the latter substances; by that of the œnanthic and azoleïnîc acid; by that of the bitter almond oil, and that of the sulpho-pioramyls; by the constitution and properties of xanth-oxide and uric acid, and by the circumstances under which these bodies are pro-

duced ; by the analogy of constitution of several chlorides of compound radicals, destitute of oxygen, and of the oxides of similar radicals ; by that of the indenigen and indenoxide ; by the various stages of oxidation of isaten, &c. ; by the action of sulphuretted hydrogen on the nitrites of naphthalin and protoxide of benzin, of which are produced the amidures of the radicals ; of these bases are produced— $(C^{20}H^{14}O + \ddot{N}) + 6H^2S = (C^{14}H + Ad) + 4\dot{H} + 6S$, $(C^{12}H^{10}O + \ddot{N}) + 6H^2S = (\bar{C}^{12}H^{10} + Ad) + 4\dot{H} + 6S$. Finally, it is known to chemists that the constitution of the combinations formed by kakodyl, was understood by the illustrious Swedish chemist, at the time, when similar combinations were considered as composed in a manner totally different from that now believed to be the true one ; induced by which circumstances the celebrated Bunsen attempted to isolate this radical.

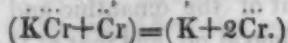
34. Great, however, as the number of facts be, apparently warranting the truth of the hypothesis in question, it may, perhaps, not hold good in all cases, as it starts from a principle admitted in organic chemistry, viz., that *each oxygen combination of the first order is an oxide of a radical*, a principle found to be incorrect with reference to



and in many others.* Notwithstanding, therefore, the most plausible analogies, Berzelius, not to be contradicted by his own hypothesis, considered these bodies as combinations of the third and second order. The combination of H. Rose, for instance, is, according to the Swedish chemist, composed of sulphuric acid, and chloro-sulphuric acid.



And Peligot's salt would consist of



With reference to Pelouze's acid, it might have been

* The sign ' means one equiv. of chlorine.

considered as something analogous to the sulphate of oxide of nitrogen; but since I have shown that the sulphuric acid does not enter into a combination with the oxide of nitrogen, and that the sulphurous acid, with regard to sulphur, acts the part of a radical, it became necessary to consider these combinations as well as oxynitro-sulphuric acid as being constituted in a manner analogous to that of the oxy-sulphuric acid.

35. Like the combinations of this kind, the benzamid also, and the oxamid, salicylamid, phtalamid, and other analogous oxidated combinations are composed of two radicals. Oxygen, therefore, may contribute to the production of compound radicals, and these, by combining with oxygen, chlorine, and sulphur, &c., may form oxy-acids, oxy-chloro-acids, oxy-sulpho-acids, oxy-bases, oxy-chloro-bases, oxy-sulpho-bases, and, finally, combinations also, in which either the oxygen, the chlorine, or the sulphur are no less acidifying agents than as means of reproducing bases.

The chlorine or the sulphur, however, being able to behave as the electro-negative element with reference to the oxygenous radical, and the oxygen itself, relative to a similar radical, acting the same part, it follows that, in an organic combination, the whole amount of oxygen is not employed in the formation of bases and acids, into the composition of which enters neither chlorine nor sulphur, nor any other substance acting relative to a radical as an electro-negative principle. The hypothesis, therefore, laid down by Berzelius, like the principle upon which it is based, may sometimes be found insufficient. A strange relation between two sciences, both purporting the study of bodies, which, though dissimilar in nature, yet are formed and changed according to the same laws, the same principles, and often, even, according to the same theories. This stamps the hypothesis of the Swedish chemist with a degree of probability which is wanted in that of his opponents; asserting that the hyponitric acid in compound radicals,

may displace the hydrogen without being able to show that this acid acts the part of a simple body.

On the Constitution of the Hyponitric Acid.

36. Comparing the property of nitrous acid to combine with sulphuric acid, with that of the said acid to form with nitric acid hyponitric acid, and considering the fact that the latter acids may be decomposed by bases, Berzelius at first supposed that these combinations are composed of nitrous and nitric acids.

37. When H. Rose, however, was believed to have prepared the sulphate of oxide of nitrogen, the Swedish chemist, in accordance with the German, considered the hyponitric acid of a constitution analogous with that in question. Both these views not well agreeing with the laws of multiple proportions, it remains to ascertain whether the hyponitric acid is a particular stage of oxidation of nitrogen.

38. If from motives on which the first hypothesis is based, the hyponitric acid is composed according to $\ddot{\text{N}} + \ddot{\text{N}}$, the nitrous acid ought to consist of $2\ddot{\text{N}} + \ddot{\text{N}}$, owing to the influence which an excess of oxide of nitrogen has on nitric acid, and to the property of the acid formed in this reaction, by which, on being put together with water, it may be resolved into the binary combinations of which it was formed. The nitrous acid, however, in contact with the hydrochloric acid, forms no chlorine. It, therefore, contains no nitric acid, from which we may conclude that the hyponitric also contains none.

39. If the hyponitric acid would be composed according to formula $\ddot{\text{N}} + 2\ddot{\text{N}}$, then, by the action of hydrochloric acid on a solution of this acid in concentrated sulphuric acid, oxide of nitrogen ought to be disengaged, which, however, does not occur.

40. The question may be resolved in another manner, by

starting from stableness, when two points are to be considered. The first is the relative stableness of combinations $\ddot{\text{N}}$ and $\ddot{\text{N}}$, and the second that of the acids $\text{H} + \ddot{\text{N}}$ and $\ddot{\text{N}} + \ddot{\text{N}}$ or $\ddot{\text{N}} + 2\ddot{\text{N}}$.

The greater stableness of $\ddot{\text{N}}$ relative to $\ddot{\text{N}}$ may be attributed to a cause similar to that by which the relative stableness of combinations $\ddot{\text{N}}$, $\ddot{\text{N}}$, $\ddot{\text{N}}$, $\ddot{\text{N}}$, is produced. It may likewise be ascribed to the affinity of $\ddot{\text{N}}$ to $\ddot{\text{N}}$ or $\ddot{\text{N}}$.¹ In the latter case, the hyponitric acid is a particular stage of oxidation, but it is not such a one in the second case.

If this acid is composed according to the formula $\ddot{\text{N}} + \ddot{\text{N}}$ or $\ddot{\text{N}} + 2\ddot{\text{N}}$, it must be more stable than $\text{H} + \ddot{\text{N}}$, as the former may be formed by the action of oxide of nitrogen on the second, and because the stableness of a combination depends on its affinity; or it is proportionate to the affinity of the binary combinations, of which these combinations are constituted.* The foregoing observations and considerations, having shown that the hyponitric acid is less stable than the hydrated nitric acid, it follows that it is not a combination of nitric acid with nitrous acid or oxide of nitrogen.

Ibid. from Poggendorff's Annalen.

*Supposing that the bodies are under the conditions stated in the said case.

ART. LXXIV—ON THE POWER OF DISSOLVING OXYGEN,
POSSESSED BY LITHARGE IN A STATE OF FUSION, AND
ON SEVERAL PECULIARITIES WHICH ACCOMPANY THE
PRODUCTION OF LITHARGE BY CUPELLATION ON A LARGE
SCALE.

By M. F. LEBLANC.

WE know that the cupellation which is practised in establishments where lead is prepared from the ore, is an operation, the object of which is to separate the silver from the lead, by eliminating the latter metal in the state of an oxide. Cupellation in the large way, or refining, as it is called, in some manufactories differs from the cupellation of the assay offices, on account of the litharge, or protoxide of lead being formed by the action of the oxygen of the atmosphere on the lead in a state of fusion at a high temperature, instead of being eliminated by absorption into the substance of cupel, it flows out of the furnace as fast as it is produced along a kind of gutter, which is constantly kept level with the surface of the melted metal. The substance that forms the cupel of the furnace, ought, as much as possible, to resist the absorption or dissolving action of litharge in a state of fusion.

The oxygen of the atmosphere is projected on the surface of the metal by a forced current of air.

During a visit I lately made to Poultaouen, I had an opportunity of being present at many of the operations for the refining of lead, containing silver, and of making several observations which perhaps will appear not devoid of scientific interest.*

* The process of refining at Poultaouen is usually performed upon about a ton of lead at a time; at the end of about eight or ten hours the fusion is complete, and they begin to skim the pot: soon afterwards

We know that the litharge of commerce should possess certain characteristics, which can be produced at will to a certain extent, by properly managing the duration of the time allowed for the cooling of the litharge that flows from the furnace. It is known that litharge when cooled quickly is yellow, or greenish yellow, and that litharge when slowly cooled, under the circumstances pointed out by M. Fournet, changes its structure and color, and acquires properties which cause it to be much sought after in commerce.

It is to the study of the physical and chemical modifications that produce this transformation, that I devoted myself.

M. Fournet admits, in effect, that litharge in fusion can absorb oxygen, by becoming super-oxidised, and that at a higher temperature than is necessary for the decomposition of minium. This philosopher admits that the red litharge so much sought after in commerce owes its properties to an excess of oxygen.

The opinion of M. Fournet is not shared by M. Thénard; this illustrious chemist repudiates the hypothesis of the super-oxidation of lead, at the temperature of the furnaces, cupel, and considers it possible that a solution of the oxygen in the litharge, analogous that of the same gas in melted silver, takes place. Thus oxygen unites itself to the protoxide of lead when the cooling process is slow, and disengages itself when it is rapid.

M. Pernolet, the present director of the mines and workshops at Poultaouen and Huelgoat, had previously observed that litharge in fusion held a gas in solution, varying at

the draught of air is employed, and the *obstricks*, or black litharge, begins to pass over, it is a protoxide of lead mixed with oxysulphurets. The time occupied in the passing of the black litharge, varies according to the degree of the purity of the lead; it may continue for sixteen or twenty hours before they begin to collect the litharge of commerce. The total duration of the process for the refining of a ton of metal, is from 48 to 50 hours.

different periods of the process, and that this gas had a tendency to disengage itself at the instant the solidification took place. The facilities he was kind enough to grant me, enabled me to collect, carefully, the litharge, in different degrees of purity, and at various stages of the process; I also collected the gas when it was disengaged. The experiment completely confirmed the suspicions of M. Thénard, so far as regards the solution of the oxygen; for the gas collected offered me the properties of nearly pure oxygen. Its analysis indicated from 82 to 90 per cent. of oxygen. It cannot be said with certainty that the proportion of nitrogen was not due to the accidental presence of a small quantity of air; in fact, when repeating the experiment in the same manner upon silver taken out of the refining cupel, I did not find more than 90 per cent. of oxygen absorbable by heated phosphorus.

The quantity of oxygen dissolved in a given weight of litharge is too considerable to enable us to admit that the silver contained in the litharge could be the solvent of the gas; this proportion was not less than 50 cubic centimetres per kilogramme, notwithstanding the losses inseparable from the mode of operating. Besides, the last quantities of the litharge, and the richest did not contain more than 0.001 to 0.0015 of silver.

It appears to me, therefore, an established fact that litharge, a substance incapable of oxidation at the temperature of the furnace, might, under the influence of a current of air, dissolve the oxygen after the same manner as silver, and act as most liquids do when in contact with gases.

The black, or impure litharge is, according to my experiments, unfit for dissolving the gas; at least the quantity found was so trifling, that we may be allowed to consider its presence as accidental; analysis has also indicated oxygen and nitrogen, in nearly the same proportions as in the air. This circumstance will not be surprising, if we reflect

that this excess of litharge contains sulphuretted, oxidisable elements.

Ought the solution of oxygen in a liquid in igneous fusion, and possessing no chemical action on the gas, to be considered as a general phenomenon, or merely confined to litharge and silver? It is a question, the experiments I propose to make may perhaps solve. The phenomenon is connected, perhaps, with questions arising out of geology, and consequently deserves an attentive study.

Not to wander from the subject of this note, I shall confine myself, for the present, to the examination of what passes in the centre of the masses of melted litharge when it leaves the furnace, and to the discussion of the part the imprisoned oxygen may play in these masses that become solidified, and end in changing, by degrees, their internal structure.

At Poultaouen, the litharge, when it leaves the furnace, and when it has acquired a sufficient degree of purity, is collected in iron pots of a conical form, and holding about 30 litres. The litharge is not long before it becomes solid on the surface, and it is then of a yellow or greenish yellow color; at the end of a few hours, sometimes at the end of half an hour, the mass breaks and splits in every direction, becoming a friable crystalline mass, possessing a deep red color; the crust, which had become suddenly solidified, alone preserves its color and coherence. The red litharge only, which is carefully picked out, is fit for sale; the yellow litharge is placed apart, to be revived.

Sometimes the phenomenon takes place more quickly; a sort of explosion occurs, which, in the first instance, separates the conical mass of litharge into a number of large blocks, at the same time there is a projection of a certain quantity of litharge, which had remained liquid, or in a pasty state in the interior.

It appears to me to be probable enough that the oxygen imprisoned while the solidification was going on, acts me-

chanically in the phenomenon of the exfoliation of the litharge.*

It is proper to point out the fact that all those circumstances that tend to diminish the rapidity of the cooling process, and the solidification of the litharge, have also a tendency to increase the proportion of red litharge that is formed; when it is poured into vessels of insufficient capacities, the litharge cools too quickly, and remains yellow, and without exfoliation.

M. Fournet admits that red litharge contains more oxygen than yellow, and that it owes its color to a certain proportion of minium, a portion of which many specimens have exhibited the undoubted presence of.

M. Thénard, and most chemists, also, attribute the color of the litharge of commerce to the presence of a small quantity of minium.

Without wishing to deny that litharge, when slowly cooled, cannot, under certain circumstances, absorb oxygen and form minium, a well established fact I think, nevertheless, I am able to demonstrate that another explanation must be found for the exfoliation of the masses of litharge, and the production of red litharge. The following are the experiments on which I think I can rest this assertion:—

1. The red litharge I have examined gave out no oxygen by heat.

2. The same litharge tried with much care by pure nitric acid, furnished me with no puce-coloured oxide; a minute portion of minium added to yellow litharge, scarcely modifying its tint, could be discovered under the same circumstances.

3. The red litharge, heated to a temperature at which it gave out no oxygen, and thrown suddenly into water, became yellow.

* The first pots of litharge that are collected do not always exfoliate; nevertheless, I have proved that they sometimes contain oxygen in the state of gas, although in small quantities.

This experiment shows that the variations in the structure and colour of litharge, according to the circumstance of temperature that accompany its production, do not depend on changes in chemical composition, but much on modifications arising out of isomerism or dimorphism, like those that cause the difference between vitreous arsenious acid, and opaque arsenious acid, barley-sugar and sugar-candy, red iodide, and yellow iodide of mercury, &c.!

These modifications in the structure and color of protoxide of lead have a relation to the density of the specimens. According to the experiments I have made, red exfoliated litharge is less dense than yellow crystallised litharge. Figures having connection with various experiments made for this purpose, will be found in my *Memoirs*.

In fine, the facts related in this note appear to me to establish—

1. That oxygen can be dissolved by litharge in a state of fusion, as it is dissolved in silver, and that it does not form a super-oxidized combination: the nitrogen dissolves in it, *perhaps* in a small proportion.

2. That physical differences of structure, color, and density alone exist between yellow and red litharge, which make no alteration in their chemical composition. The different varieties may be produced at will by a dry process, according to the circumstances of temperature, and the quickness of the cooling of the mass.—*Ibid.* from *Jour. de Phar.*

ART. LXXV.—MANNA.

By A. LEUCHTWEISS.

MANNA has been examined by Fourcroy and Vauquelin, Thénard, and Buchholz. The latter found in the best manna :—

Mannite,	- - - - -	60
Mucous sugar and coloring matter,	- - - - -	5.5
Gummy extractive,	- - - - -	0.8
Gum,	- - - - -	1.5
A glutinous matter,	- - - - -	0.2
Water,	- - - - -	30

Thénard describes manna as containing mannite, 10 per cent. of fermentable sugar, and a nauseous uncrystallisable substance; the latter may be separated by means of æther. To obtain pure *mannite*, the sugar must be separated by fermentation, the filtered solution evaporated, the residue dissolved in boiling alcohol, of 0.833 specific gravity, when the mannite separates on cooling. By washing with cold spirit, it is obtained beautifully pure and white. Manna yields in this way from 32 to 42 per cent. of mannite.

The analysis of three specimens gave :

	I.	II.	III.
Water	11.6	13	11.1
Insoluble constituents (impurities)	0.4	0.9	3.2
Sugar	9.1	10.3	15
Mannite	42.6	37.6	32
Mucilage resin, an acid and nitrogenous matter	40	40.8	42.1
Ash	1.3	1.9	1.19
	<hr/>	<hr/>	<hr/>
	100	100	100

The ashes of manna consist of potash, lime, magnesia, peroxide of iron; phosphoric, muriatic, sulphuric acids, in minute quantities; and alumina and silica, probably from impurities.

The mucilage in manna is the same as ordinary mucilage. The sugar is crystallisable grape sugar. The resin and acid are soluble in ether.—*Ibid.* from *Liebig's Annalen*.

ART. LXXVI.—A NEW CAUSTIC FORMED BY THE MIXTURE
OF SAFRAN (PEROXIDE OF IRON) WITH SULPHURI
ACID.

By M. VELPEAU.

DURING a series of experiments, to which he had for some time devoted himself, on the action of various powerful caustics, M. Velpeau at length arrived at sulphuric acid, solidified by safran, a combination that appeared to have the most happy results. To concentrate the sulphuric acid under the form of a ductile paste, or rather a soft pommade, not capable of extending beyond the limits he had traced out, he had to make a host of attempts and trials; it was necessary to discover a body or bodies which, combined with the liquid mineral, could form a concrete, without depriving it of its caustic properties. Asbestos, charcoal, flour, and various other substances failed. At length he came to safran, which incorporates easily, and in sufficient quantity to make a pommade of a proper consistence. This substance being carbonized by the acid, a paste of a beautiful black color is the result, reminding one of China ink or dried blacking. This paste is placed in a china vessel; the surgeon takes it up with a spatula and spreads it over the ailing spot as he would soft cerate; he forms a layer from two to four millimetres in thickness, more or less, makes the edges round and circumscribes the limits to the actual seat of the disease, leaving it exposed to the air for some time until it is dry.

A crust is soon formed, and it is then covered with a compress and bandage. The caustic that remains in the vessel cannot be preserved for any length of time. The sulphuric acid attracting powerfully the humidity of the air; but that which has been applied to the flesh forms a hard crust, and sounds, when struck, like charcoal, perfectly dry, bounded by the limits to which it has been applied, and of a depth equal to the thickness of the layer that was applied.

The slough began to detach itself from the eighth to the tenth day in the case of an individual who had submitted to its limited application. In the instance of a patient who had a cancer, and in whose case 100 grammes of the caustic pomade had been used, it was noticed with satisfaction that no symptom of re-absorption took place, and that, in addition, the caustic had the effect of completely removing the disgusting smell the cancer had hitherto possessed, and with which it infected the sick person and those near him. The cauterized tissues even gave out an odor rather agreeable than fetid. While waiting until additional instances shall enable us better to appreciate the value of the new agent, we ought to direct attention to the three important conditions it offers: namely, 1st, the exact circumscription of its action to the limits marked out by the pomade; 2d, the quick separation of the slough; and 3d, the absence of serious re-absorption.—*Chemist.*

ART. LXXVII.—MODE OF PREPARING EPISPASTIC PAPER

By WISLIN.

THE great use made at the present day of epispastic paper, in the healing of blisters, the good effects that have arisen from it, in addition to the facility of its application, have brought this preparation into great favor; still, as the mode of manufacturing it was unknown, it remained a monopoly for a few of the pharmacopolists of the capital. I am only speaking here of the method employed for spreading the composition on the paper, not of the composition itself, most books of instruction containing several formulæ.

Every treatise on pharmacy, even the most recent, direct the employment of the common spatula, an impossibility when you consider the consistence of the matters employed, which will always be, according to the temperature, either too fluid or too solid, and they can never preserve their fluidity like various compositions employed in the making of plasters.

As we know that all these epispastic preparations have for their base hog's lard and bees'-wax, a substance which has never more than middling consistence, and passes, without transition, from excessive fluidity to a consistence too solid to be spread by the spatula. On this account, after having vainly attempted this method, I proceeded in search of another, and the following is a plan by which I was successful :—

After having prepared a number of strips of fine white paper, not much sized, 6 centimetres 3 millimetres in width, and 45 centimetres in length, I melted the epispastic composition in a plate, placed above a vessel of boiling water; I took the extremity of one of the bands of paper in the left hand, while, with the other hand, I held the other end of the paper raised in such a manner that described the arc of

a circle ; then I brought the under side of the paper close to the composition, and made it glide rapidly over the surface, taking particular care that the composition, which ought only to cover one side of the paper, does not touch the other. A little practice enables one to avoid this easily.

While the paper, guided by the left hand, passes over the surface of the composition, the right hand follows the movement, and lowers the other extremity when it arrives at the end ; the paper, still supported by the left hand, finds itself thus placed horizontally above the plate, in which position it is held until it grows cold, the work of an instant only.

As fast as the papers are prepared they are ranged on a table by the side of each other, but in a few minutes afterwards they may be placed on the top of each other, without fear of their adhering. They are then cut up with a pair of scissors, and each strip of paper, of the dimensions we have described, will just make 5 pieces.

By varying the temperature you can change this paper at your will with more or less of the composition ; so that, when you wish for a thin layer, you take care to keep the water boiling ; if, on the contrary, you require a thicker layer, the heat must be below 100° C., which can be easily managed by interposing a plate between the boiling water and that which holds the composition ; if it be required to be still more loaded you pass it a second time over the composition.—*Ibid.*, from *Journ. de Chem.*

ART. LXXVIII—CONTRIBUTIONS TOWARDS THE CHEMICAL HISTORY OF THE GRATIOLA.

By M. EUGENE MARCHAND, OF FECAMP.

THE gratiola (*Gratiola officinalis*, L.) *hedge hyssop*, is a plant endowed with purgative powers of the most energetic nature, and on this account it is sometimes used as a popular medicine, under the title of "the poor man's herb." Looking at it as one of the most active and most dangerous plants that grow in France, we ought to be astonished it has not, long since, attracted the attention of pharmacopologists and chemists; for one only, the learned Vauquelin, published, in 1809, the result of his inquiries into its constitution; but the means science, at that time, had placed at the disposal of the chemist were far from reaching the perfection and precision organic analysis has attained since that epoch. We must not, therefore, be astonished if plants, analysed at the beginning of this century, exhibit to the chemist of our day, who analyses them anew, principles of which his predecessors were far from even suspecting the existence. Having mentioned this to justify myself for having ventured to undertake, afresh, the analysis of a plant that merited the honor of being examined by Vauquelin, I shall endeavour at present to demonstrate, that the extremely bitter *resinoïd* matter, known to exist in the gratiola, and to which its properties are attributed, is not the direct principle, but a complex substance, a part of which only communicates to it its medicinal energy.

But, before we proceed further, let us examine the list of the principles Vauquelin detected in this plant. These were an extremely bitter *resinoïd* matter, an animal matter, a brown-colored gum, a vegetable acid, which Vauquelin believed to be either malic or acetic, and which was in combination with soda and lime, phosphates of lime and iron,

oxalite of lime, chloride of sodium, silica, and woody fibre *Vauquelin, Bulletin de Pharmacie, t. i. p. 481.*)

It may be observed that Vauquelin has not mentioned tannic acid among these principles, and yet it exists in the gratiola. This was because, at the time Vauquelin undertook his task, men had extremely vague ideas of the constitution of organic substances, and on the characters they could offer in their reciprocal combinations. Although science has not as yet had the last word on the subject, it is at least permitted to us, in a host of instances, to dissect nature in a better manner, and thus be able to discover laws and substances she so obstinately conceals from us.

The whole of the tannic acid that exists in the gratiola is found in the resinoid substance obtained by Vauquelin, and it exists in combination with other principles, among which is found one at least which ought to take its place near digitaline. In fact, if we dissolve in alcohol the resinoid matter of Vauquelin; if we add it to the liquid sulphate of iron, until it becomes tinged with blue; if we add to this mixture as much hydrate of lime as is necessary to saturate the free sulphuric acid, and decompose the excess of sulphate of iron that was used; if we mix the alcoholic liquor with the water, for the purpose of afterwards filtering it (after having bleached it by means of animal charcoal, if necessary;) then, if the liquor is evaporated in *vacuô*, or rather in a situation where the aqueous vapor shall be constantly carried off by concentrated sulphuric acid, we shall obtain as a residuum a white matter; but still a compound substance.

This substance, by the addition of water, is partially dissolved, and gives an excessively bitter taste to the liquid. The intention in adding the water is to remove the mineral saline particles that are often, if not always, mixed up with the bitter principle of the gratiola, in this first part of the operation.

What remains after being washed in water is a substance

easily reduced to powder. When hydrated ether is added to this, it softens, and is partly dissolved; while the portion that remains undissolved collects at the bottom of the vessel in the form of a syrup; this liquid separated from the layer of ether that floats over it, and dissolved in alcohol remains unclouded, and, if after thus having been mixed with the alcohol, it is left in the open air, we obtain, when the liquid has evaporated, a white mass, in which you may perceive a number of minute globules, resembling papilæ. This substance, in my opinion, bears the same relation to the gratiola, as the digitaline does to the digitalis, and I think I am authorized in proposing for it the name gratioline, or, better still, gratiolin, to show that the substance is not an alkaloid, for the termination *ine* ought, in my opinion, to be reserved exclusively for that class of bodies.

Whatever may be the fate of this proposition, I shall no longer dwell upon it, but continue the enumeration of the characters this new principle presents.

It appears under the form of a white mass, made up of minute grains; it is to a very small extent soluble in water, to which it, nevertheless, imparts a very bitter taste, which, as in the case of digitaline, is particularly sensible at the back of the mouth; a small quantity of alcohol renders it rather more soluble in this liquid; alcohol dissolves it easily, and the liquid becomes milky when mixed with water; it is, to a certain extent, soluble in ether.

Placed in water, and submitted to the action of heat, until the water boils, it softens and collects on the surface under the form of a small oily drop.

Placed in a capsule of platinum, and heated in an open fire, it softens, swells, melts, becomes colored, is inflamed, burns with smoke, and at last leaves a residuum of black charcoal, which disappears by continuing the calcination. But I must still observe that, after this calcination, a small quantity of white ashes remain.

Sulphuric acid turns gratiolin yellow, and, while dissolv-

ing, it acquires a purple color; the solution does not turn green when mixed with water, but it makes it rather cloudy and becomes discolored.

Allow me, in connexion with this reaction, to offer a few reflections on the red color many bodies assume under the influence of concentrated sulphuric acid. It is sometime since M. Raspail pointed out, as a property characteristic of sugar, the power that substance possessed of developing a beautiful red color, when, after being mixed with albumen or oil, it is submitted to the action of concentrated sulphuric acid. More recently still, M. Pettenkofer observed, that when, in this experiment, you substitute biline for the albumen or oil, the red color still appears. As early as in 1838, the first of these two chemists, speaking of the red color salicine always assumes when in contact with sulphuric acid, gave this opinion, that salicine might perhaps be merely a combination of sugar, and a principle which he denominated *resineux*, and which in this case might answer the purpose of exciting the characteristic reaction of sugar. Since that time, distinguished chemists have added their authority to the opinion of M. Raspail; for, in 1839, M. Liebig was led to consider salicine as a combination of grape sugar and saliretine. More recently, M. Piria was induced, in his turn, after a series of very remarkable experiments, to consider the same body (salicine,) as a combination of sugar with another substance, discovered by himself, and to which he gave the name of saligenine. As we see, then, let the constitution of salicine be what it may, chemists always agree that sugar is one of its elements, and the opinion of M. Raspail is entirely confirmed.

Passing, then, to digitaline and gratioline, which also assume a beautiful red color when in contact with concentrated sulphuric acid; recollecting that these bodies, like salicine, are neutral substances, would it not be right to presume that sugar enters also into their constitution? I know that this question can only be resolved when we well

understand the elementary composition of these substances; but it is a subject of study which, it appears, must lead to interesting results, and it would be desirable that chemists placed in favourable situations to undertake such a task would busy themselves with it. I am persuaded they would be amply repaid for their trouble.

After this digression, I again take up the description of the chemical characters of gratiolin.

Nitric acid dissolves it without discoloring it.

Chlorohydric acid dissolves it, and it assumes a yellow color.

Caustic potash communicates a dirty green color to it, which afterwards passes into a greenish yellow, and finally into white.

Caustic ammonia communicates to it a blue color, well marked, but without being beautiful. The reaction quickly takes place, and in a short time the mass again becomes white. It is useful to observe that, under the influence of these two agents, gratiolin does not dissolve in the alkaline liquor.

The extract of oak galls precipitates gratiolin from its watery solution, if the latter is perfectly neuter or slightly alkaline. If it is alkaline, the precipitation does not take place, for the tannate of gratiolin is soluble in liquor ammoniæ.

The ethereal liquid, of which I have spoken above, having been evaporated, has left, as a residuum, a white uncrystallised substance, slightly bitter, insoluble in water, soluble in alcohol at 104°, capable of being precipitated from this solution by water, soluble also in ether. This substance is acted on by fire in the same manner as gratiolin, from which it differs, however, inasmuch as concentrated sulphuric acid slowly dissolves it, acquiring a yellowish-brown color, slightly tinged with red. But everything induces me to believe that the color developed under these circumstances would be simply yellow, if the substance on

which we are engaged were not accompanied by a small quantity of gratiolin which, as we have already seen, is slightly soluble in ether.

In a forthcoming paper, I shall return to the chemical and therapeutical properties of gratiolin, and give the result of my inquiries into the chemical constitution of the gratiola.—*Ibid from Jour. de Chimie.*

ART. LXXIX.—ON A REMARKABLE CHANGE WHICH MORPHINE UNDERGOES BY THE ACTION OF SULPHURIC ACID.

By A. E. ARPPE.

WHEN morphine is dissolved in an excess of sulphuric acid, and the liquid evaporated to incipient decomposition, a white body is separated by adding water to the brownish mass, which is not sulphate of morphine, and does not contain a trace of morphine.

This white body is most readily obtained in the following manner :—Crystallized sulphate of morphine is treated with a slight quantity of dilute sulphuric acid, the mass evaporated and heated to 302°–322°. The brown mass thus obtained is boiled with water, so that the precipitate which had formed on the addition of water is entirely redissolved. The solution is filtered as hot as possible, when the white body again separates if the solution was sufficiently concentrated. That portion of the brown mass which was not taken up by the water is again treated in the same manner; a few drops, however, of sulphuric acid should be added, in order to produce a perfect solution on boiling. When a sufficient quantity of sulphuric acid has been used, and the stated temperature has not been exceeded during the evaporation,

the precipitate formed is perfectly white, while the supernatant liquid is nearly colourless, and the filter is only coloured by a minute quantity of a light brown body. The white substance, collected on a filter, may be easily washed with cold water from the excess of sulphuric acid; it is then freed from adherent moisture by means of blotting-paper, and finally dried at a very gentle heat. The mother-ley contains a little more of the substance in solution, but it only yields a very impure preparation on evaporation.

The following are the properties of this body:—Its colour is white, and, after drying, always more pure than in the moist state, yet frequently with a brownish tint, which is generally not to be removed by the ordinary means. Suspended in the liquid, it separates readily in large caseous flakes, and on evaporation shrinks extremely. As seen under the microscope with a magnifying power of 200, it consists of round shining globules, which are perfectly homogeneous, but not in the least crystalline. Exposed to the air, it gradually becomes greenish on the surface; it is slightly soluble in water, but the solution is decomposed on boiling, and acquires an intense emerald-green colour. It is not dissolved or altered by alcohol or æther. In acid liquids, especially if sulphuric or muriatic acid is present, it is dissolved with the greatest ease without change; the substance separates unaltered on evaporating the dilute solutions, but it is decomposed by the concentrated acids with formation of a brown body. Alkaline fluids, especially when caustic and concentrated, act in a similar manner to the concentrated acids; they destroy the substance, and give rise to the formation of a brown product of decomposition.

Potash and ammonia produce in the acid solutions very considerable precipitates, which are readily soluble in an excess of the precipitant. Carbonate of ammonia likewise yields a precipitate, but does not redissolve it. These precipitates are especially characterized by the circumstance,

that they soon acquire, when exposed to the air, a more or less dark green colour, being converted into another body which contains only two-fifths of the sulphuric acid of the white substance. The amount of sulphuric acid of this white substance is greater than that of the sulphate of morphine, but only a portion of the sulphuric acid is separated from a solution in muriatic acid by chloride of barium, while the other portion can only be detected after decomposition by chlorine. The analysis of the body, dried in a current of carbonic acid gas, yielded—

		Found.	Calculated.
Sulphuric acid	-	14.65	14.14
Carbon	-	61.12	61.22
Hydrogen	-	5.88	5.58
Nitrogen	-	3.86	..
Oxygen	-	..	14.01

The organic constituent of this compound is, judging from its equivalent, equal to 4 atoms of morphine; it may consequently be expressed by the formula $4(C^{35}H^{26}NO^6) + 5SO^3$. If we set out from the supposition that the morphine is a conjugated compound of ammonia, its sulphate, which contains, like the salts of the organic bases in general, 1 atom water, can be expressed by the formula $C^{35}H^{17}O^6 + NH^4O, SO^3$, i. e. it contains 1 atom of oxide of ammonium instead of the ammonia. On being heated with sulphuric acid the whole of the water is expelled, and the peculiar sulphates of ammonia discovered by H. Rose are formed, in which the ammonia is conjugated with the sulphuric acid. Of these compounds the neutral is NH^3SO^3 , and the acid one which Jacquelin analysed $3NH^3 + 4SO^3$. If these two salts were formed in the substance examined, it is directly evident that the above composition must result, and the rational formula would accordingly be $(C^{35}H^{17}O^6 + NH^3) + SO^3 + 3(C^{35}H^{17}O + NH^3) + 4SO^3$. The fact that anhydrous sulphuric acid passed over effloresced morphine produces this body speaks in favor of this view; nevertheless the change which

the morphine undergoes must be more considerable, since it can no longer be separated from the compound. Moreover, the circumstance that a portion of the sulphuric acid is precipitated by chloride of barium, while in the above ammonia salts none of it is thrown down, cannot be brought into perfect union with the view above mentioned; it might however be explained by a decomposition being perhaps effected by the acid employed to dissolve it.—*Chem. Gaz. from Ann. der Chem. und Pharm.*

ART. LXXX.—OBSERVATIONS ON THE THEORY OF M. PELIGOT AND M. BAUDRIMONT RESPECTING THE MANUFACTURE OF SULPHURIC ACID.

BY DR. KÖNE.

IN the 'Comptes Rendus,' vol. xix. No. 9, is a treatise by M. Peligot, the object of which is to prove,—1st, that in the manufacture of sulphuric acid, the sulphurous acid acts *incessantly* and *exclusively* on the nitric acid, with formation of sulphuric acid and hyponitric acid; 2d, that the formation of sulphuric acid is quite independent of the presence of the crystals in the lead-chambers.

This investigation has given rise to a dispute as to priority between the above chemist and M. Baudrimont, who likewise supposes that the hydrated nitric acid (*azotate hydrique*) is absolutely requisite for the formation of the sulphuric acid.

Both these chemists therefore agree that the sulphurous acid reduces the nitric acid merely to the state of hyponitric acid.

But from my investigations concerning the nature of the crystals which form in the lead-chambers, it results that the sulphurous acid reduces the hyponitric acid to nitrous acid. This result, which led me to consider the theory of M. de la Provostaye as incorrect, induces me also to show that that of M. Peligot is erroneous.

M. Baudrimont adopts, with the followers of the theory of M. Gaultier de Claubry, that the crystals, or at least an analogous compound, is indispensable to the formation of sulphuric acid; but this theory does not answer to the facts; for, as M. Peligot has proved, sulphurous acid is capable of deoxidizing nitric acid in the presence of a considerable quantity of water. This proves that the compound ($\text{SO}^3 \text{NO}^3 + \text{SO}^3 \text{HO}$) is not absolutely requisite, as was hitherto supposed, for the formation of sulphuric acid.

The sulphurous acid acts under these circumstances, deoxidizing precisely like hydrochloric acid, with which it possesses the same property in respect to nitric acid, and in almost the same degree. As long as the latter is not too diluted, the first two convert it into nitrous acid, which is decomposed into nitric oxide and nitric acid, if there is sufficient water present; but in the manufacture of sulphuric acid the quantity of water is seldom large enough for this change to take place, for it is not to the interest of the manufacturer to exclude from action one of the generators of his product, nor to convey more water into his lead-chamber than requisite for the formation of the acid; nor is it more requisite that he should introduce dilute acid into his large chamber at the commencement of the operation; it suffices if there be a sufficient quantity of aqueous vapour present to prevent the formation both of crystals as well as of nitric oxide. The reaction goes on regularly, and the product only contains traces of nitric acid; but then follows the reaction between sulphurous acid, nitric and hyponitric acid; for the hyponitric acid, which is produced by contact with sulphurous acid, instead of being oxidized and converted

into a hydrated acid, forms under these circumstances, on the one hand nitrous acid, and on the other sulphuric acid as my experiments have shown.

In a leaden chamber in operation, the sulphurous acid therefore reduces the nitric to nitrous acid without the formation of crystals, the quantity of water being too large for the compound ($\text{SO}^3 \text{NO}^3 + \text{SO}^3 \text{HO}$) to be produced, and too small for the nitrous acid to be decomposed into nitric oxide and nitric acid.

When the latter case occurs, which happens sometimes under circumstances that must be regarded as accidental, the product is impurified with larger or smaller amounts of nitric acid, from which it is freed by passing sulphurous acid through it. This operation can never fail to succeed, because such an acid contains sufficient water for the nitrous acid to be decomposed into nitric oxide, which escapes, and into nitric acid, which is again destroyed by the influence of the oxidizing agent.

In the opposite case, when the sulphuric acid is too concentrated, the nitrous acid undergoes no further decomposition from the sulphurous acid : nor is it possible, by means of this acid, to free the commercial sulphuric acid at the ordinary temperature from nitric acid, but perfectly well from nitrous acid. The first of these acids is decomposed during the concentration into oxygen and nitrous acid, as I have shown, by allowing hydrochloric acid gas to act on the monohydrated sulphuric acid which had been employed for concentrating commercial nitric acid. No chlorine was disengaged, and thence follows, contrary to the opinion of M. Peligot, that the concentrated sulphuric acid contains neither nitric nor hyponitric acid. Nor can there be any nitric oxide contained in it, this not being perceptibly soluble in this acid; but it may contain nitrous acid, the presence of which may be readily proved, on the one hand by means of hydrochloric acid, and on the other by means of the protosulphate of iron and metallic copper.—*Chem. Gaz from Poggendorff's Annalen.*

ART. LXXXI—OBSERVATIONS ON HYPOSULPHITE OF SODA,
OR SULPHITE-SULPHURET OF SODA.

By E. MOUCHON.

THE *Abeille Medicale* for the month of June, contains an article on the hyposulphite of soda. This work deplores, as we do, the complete neglect to which this powerful agent has been subjected, and, at the same time, applauds the praiseworthy efforts that have been made with complete success by the most distinguished dermatologist of the present day, to revive the credit of an article which the praises of Chaussier and Biett ought to have protected from any unhappy influence.

While we congratulate Dr. Quesneville for the happy idea, which first occurred to him, to restore to notice an anti-herpetic, so deserving of recommendation, let us blame him for having made the plan he adopts in the preparation of his syrup of hyposulphite of soda his own exclusive property, and let us beg of him to allow us to establish a formula which shall become the property of all.

The hyposulphite of soda is by its nature, easily subjected to this species of transformation. Its great solubility in water permits us, in fact, to have recourse to that method without the least fear of failure, and every pharmacopolist, who will give himself the trouble to tax his intellect for an instant, will be able to establish a rational formula. The following is one which I think as good as that of M. Quesneville. It is extremely simple, so that it requires but an instant to reflect upon it and put it in execution.

R.—Hyposulphite of soda - - - 45 parts.

Distilled water - - - 445 “

Sugar in coarse powder - - 1,000 “

Let the hyposulphite of soda be dissolved without heat in the distilled water, add the sugar to this solution, and

dissolve it at the ordinary temperature of the air, or by means of a sand-bath, then filter the syrup through filtering paper.

Thirty grammes of this syrup will contain one gramme of hyposulphite, and this will enable you to dispense from thirty to one hundred and twenty-five grammes in the course of four-and-twenty hours.

No inconvenience appears to be attached to the use of the hyposulphite of soda, and this consideration, in addition to the incontestible advantages that result from its efficacy in cases of exanthematic affections, painful irritations of the skin, slight congestions of the viscera, scrofula, lymphatic diseases, &c. This consideration, we say, ought to be an additional element of success for this preparation of sulphur, which more strongly fortifies us in our good opinion of its future favor. As to syrup in particular, it appears to us very right to favor the employment of this agent, which we also recommend with great earnestness, because it is at present extremely easy to have it always of a well defined strength and perfectly pure, thanks to its application to the purposes of daguerreotype processes; for it must be well understood that the state of oblivion into which it had fallen, was chiefly caused by the impure manner in which it used to be prepared.—*Chemist, from Jour. de Chimie.*

ART. LXXXII.—A NEW PROCESS IN EUDIOMETRY FOR
CALCULATING THE VOLUME OF THE ELEMENTS OF
ATMOSPHERIC AIR IN RELATION TO EACH OTHER.

By M. LASSAIGNE.

SINCE the discovery of the component parts of the air, many methods have been employed by chemists to discover the relative volume of the constituent parts of this elastic fluid. The processes generally resorted to in laboratories, are all founded on the absorption of oxygen by various simple and compound bodies, whether at the ordinary temperature of the air, or by exciting the action, by caloric or electricity. In this manner the solution of sulphuret of potassium was formerly used, and afterwards phosphorus, hydrogen, and the binoxide of nitrogen have been employed, and of late years the proto-sulphate of iron, decomposed by potassium, has been recommended.

Dumas and Boussingault, by submitting air to the action of copper in a state of division, and heated to a dull red heat, has latterly produced an important modification which enables us to estimate, by weight, the oxygen and nitrogen which exist in the air, instead of calculating the volume of each of these gases, as was the case in old eudiometrical experiments.

In performing experiments, latterly, with protosulphate of iron, according to the directions of M. Dupasquier, and repeating the process he pointed out and published, we were led to adopt a test well known to chemists, but which, so far as we know, has never been applied to the analysis of air.

This method is founded on the readiness with which copper divided into thin tables becomes oxidised in contact with air, in the presence of liquid ammonia, and on the formation of a blue ammoniuret of deutoxide of copper.

Many successive experiments having shown us that this test, acting in a limited volume of air, in a very short time completes the total absorption of the oxygen contained in it, leaving the nitrogen free, we were induced to think of the application of this property to the analysis of the air; and the result has been what we expected.

The application of this new method is extremely simple, and it requires the employment of no peculiar apparatus. A common graduated tube 14 to 15 centimetres in length, and 12 millimetres in diameter, and a small phial with a ground glass stopper, containing 30 to 35 cubic centimetres, are the only vessels necessary.

The process consists in introducing into the phial from 3 to 4 grammes of copper turnings, then pouring in distilled water until the phial is half full, and afterwards filling it with a concentrated solution of ammonia. The bottle, thus completely filled, is closed with its glass stopper, and inverted in the water trough, taking care that the copper turnings do not rest on the orifice of the bottle. This first disposition being arranged, you measure a volume of air in the graduated tube filled with water, and by means of a small glass funnel it is passed into the bottle, which has been uncorked under water. This being done, the mouth of the bottle is immediately closed, and it is taken out of the pneumatic trough, and shaken incessantly for eight or ten minutes. In less than a minute or two the ammonia is seen to assume a bluish tinge, which becomes gradually darker, as the ammoniuret of deutoxide of copper is formed. This blue tint assumes its maximum of intensity when you operate on from 15 to 20 cubic centimetres of air, it then becomes gradually fainter, when all the oxygen of the volume of air on which you operate has been absorbed; this gradual loss of color, which points out the close of the operation, is due to the action of the copper, in excess, on the ammoniuret of the deutoxide, which is converted into colorless ammoniuret of protoxide.

When we have arrived at this point of the experiment, the gaseous residue is passed into the graduated tube for the purpose of measuring it, taking the precautions requisite in these kinds of operations. In the various experiments we have made, by employing the method we submit to the notice of chemists, the gaseous residue, after having been subjected to the action of the copper and ammonia, contains no trace of oxygen; for if phosphorus be introduced to detect it, it gives out no phosphorescent light in darkness, nor does it produce any diminution of its volume.

The volume of the nitric gas determined by this process, has always been two or three tenths of a degree greater than that obtained by the action of phosphorus upon the air. The proportion has been 79 : 792.2. The latter number deduced from our experiment, comes very near 79.17, which MM. Dumas and Boussingault have deduced from the most laborious analysis of the air.

When analysing an artificial mixture, composed of 41.5 air, and 57.5 nitrogen, in which the proportion of nitrogen is necessarily increased to 90.2, the new method indicates 90 of nitric gas.

The simplicity of this operation, and the short time in which it can be performed, will enable us, without doubt, to employ it in various cases.—*Ibid. from Comptes Rendus.*

ART. LXXXIII.—ON THE ACTION OF ALKALINE BICARBONATES ON VEGETABLE BASES IN THE PRESENCE OF TARTARIC ACID.

BY C. OPPERMANN.

DURING his experiments on the organic bases or alkaloïds, the chemist is necessarily obliged to make use of the generic and specific characters these bases possess, and which consist, among others, of the property of being separated by powerful inorganic bases and alkaline carbonates. In the latter instance, as we know, they often occasion, incidentally, combinations between the displaced and the displacing bases of such a nature that these reactions offer the means of distinguishing one from the other, on account of some being dissolved in an excess of the precipitating base; while others remain insoluble.

The phenomenon of the precipitation of bases by one another, when they are in the state of a salt, is not, however, a constant phenomenon. We know, by the experiments of Lasonne and Rose, that many organic substances, such as tartaric acid, sugar and albumen oppose themselves to the displacement and precipitation of an oxide, to such an extent as to resist the agency of a number of tests. M. Persoz having remarked, that, like alumina, certain organic bases possessed the property of being concealed by tartaric acid, I have endeavoured to ascertain to what extent this phenomenon was peculiar to this particular substance, for the influence such a fact might have upon inquiries into vegetable alkalis is easily conceived. I have, therefore, made experiments to ascertain whether tartaric acid, albumen, and other fixed organic bodies, possessed, or not, the property of preventing the separation and precipitation of a vegetable alkali. I shall in this place, merely give the result of my experiments on the action of the salts of morphia,

narcotia, strychnia, brucia, quinia, cinchonia and veratria, in the presence of tartaric acid, and fixed alkaline bicarbonates. The solutions of the salts I have mentioned were made in the proportion of 1 of salt, to from 200 to 500 of water (the action is precisely the same, whether we operate upon these solutions, or on decoctions of the extracts of the plants that contain these vegetable bases, provided they are properly prepared;) tartaric acid being added until the action of the acid becomes well marked, and afterwards supersaturated with one or other of the fixed bicarbonates; it appears useless to add that the acid tartrates and alkaloïds show the same result.

The salts of morphia are not precipitated by the alkaline bicarbonates, but the salts of narcotia immediately produce a considerable white easily pulverised precipitate. If we wish to be satisfied of the complete absence of narcotine in a neutral solution, we employ sulphocyanuret of potassium; this test, which produces no cloudiness in neutral solutions containing morphia, immediately causes a precipitate of a deep rose color, in those which contain narcotine, even in a quantity too small to be detected by weight. But we must always remember that a slight excess of sulphocyanuret redissolves the precipitate formed.

The salts of strychnia, under the same circumstances, either produce easily pulverised precipitates, or furnish crystals of considerable size, according to the quantities of tartaric acid, bicarbonate of soda, or potassium employed, and according to the degree of dilution; if the solution be very weak, there is no precipitate, if it be rather less so, and if it contains much tartaric acid, it still does not form an immediate precipitate by means of the two bicarbonates, but at the end of a quarter of an hour, we see very long and thin crystals appear, whose number continues to increase until all the strychnia contained in the solution is crystallised, we may perfectly satisfy ourselves that the solution contains no more strychnia or salt of strychnia, by

adding, as M. Marchand has indicated, peroxide of lead, and a mixture composed of sulphuric and nitric acids; the blue color to which a quantity of strychnia too small to be weighed gives rise, in the presence of these matters, is, as we know, a most certain sign of the presence or absence of this base; for chlorine, which M. Pelletier has recommended as a specific test for strychnia, acts in precisely the same manner on veratrine, as direct experiment has proved to me.

If the solution of strychnia is concentrated and contains but little tartaric acid, the bicarbonates immediately produce a white precipitate of a crystalline texture and the liquid no longer exhibits a trace of strychnia.

Brucia and the solutions of the salts of that base, differ completely in this respect, from the salts of strychnia; the alkaline bicarbonates produce not the slightest cloudiness.

These salts of quinine and cinchonine can also be compared and separated from one another in the same manner; the quinine cannot be precipitated when tartaric acid is present, while cinchonine is precipitated by the two alkaline bicarbonates.

In the solutions of the salts of veratria, acidified by means of tartaric acid, the bicarbonate of soda alone produces a precipitate, the bicarbonate of potash producing none.

We see, therefore, that in making use of the property possessed by tartaric acid of protecting certain bases from the action of alkaline bicarbonates, we succeed in establishing two alkaloïd groups, very distinct from each other, the first of which includes those that can be precipitated by bicarbonate of soda, and these are cinchonine, narcotine, strychnine and veratrine.

The second groups contain those that are protected from their action, namely, quinine, morphia, and brucia.

Tartaric acid also protects the infusion of gall nuts from the action of all these bases, with the exception of cincho-

nine and strychnia ; but it abundantly precipitates the five others as soon as the acid has been neutralised by ammonia ; it must be noticed, however, that an excess of this last base re-dissolves the tannate of brucia.

Besides this, we find, and this appears to me to be worthy of attention, that of the two bases which are met with in the same plant, one is constantly protected by tartaric acid, while the other is not : the employment of this method is valuable, because it allows us to separate the two bases with the greatest precision.—*Ibid. from Comp. Rendus.*

ART. LXXXIV.—CHEMICAL REMARKS ON CASCARILLA.

By A. DUVAL.

AFTER giving a brief history of this substance, and detailing the analyses of it made by Boulduc, Boehmer, Trommsdorf, Caventou, and Felix Cadet, the author proceeds to give an account of his own analysis. He says, the following are the principal substances I have found in the officinal cascarilla :—Albumen, a peculiar kind of tannine, a bitter crystallizable principle (cascarilline,) red colouring matter,* fatty matter having a nauseous odour, wax, gummy matter, volatile oil (this has an agreeable odour and a spec. grav. of 9.938,) resin, starch, pectic acid, chloride of potassium, calcareous salts and woody fibre.

The most interesting of these principles is the bitter one. My process for extracting it is as follows :—I first select a

* This is insoluble in æther, but it is soluble in alcohol, to which it imparts a fine purple colour. It readily dissolves also in water containing an alkali.

bark the taste of which is strongly bitter. After having been coarsely powdered and placed in a displacement apparatus, it is treated with water. Solution of acetate of lead is added to the mixed liquids, which are filtered and freed from excess of lead by sulphuretted hydrogen. They are again filtered, evaporated to about two-thirds; a small quantity of animal charcoal is then added, and the mixture filtered. The solution is evaporated at the lowest possible temperature. At a certain period a pellicle forms. When this has acquired a moderate consistence, and before the liquid becomes syrupy, the whole is allowed to cool, and the substance is carefully removed. Sometimes, however, it does not possess the crystalline aspect, but appears resinous, and adheres to the sides of the evaporating dish. It becomes harder by cooling.

To purify either of these substances, they are pulverized; the powder is placed in a tube, and as much cold alcohol of spec. grav. 0.870 is poured over it as is rather more than sufficient to moisten it. After a sufficient interval, this alcoholic liquid, which is highly coloured, is poured off. The greater part of the fatty and colouring matters with which the cascarilline was mixed is thus removed; the remaining powder is considerably decolorized. This is then treated with boiling alcohol of spec. grav. 0.835; a little animal charcoal is added; it is then filtered and allowed to evaporate spontaneously. The residue is dried on unsized paper. To complete its purification, it is powdered, again treated with cold alcohol, and subsequently dissolved in boiling alcohol, filtered, and allowed to evaporate spontaneously. The bitter matter is thus obtained in a state of purity.

In this state it is white and crystalline; the crystals, under the microscope, appear to be prismatic needles, sometimes mixed with hexagonal plates. It is inodorous and bitter, but this is not immediately perceptible on account of its slight solubility in water. When heated in a closed tube,

it fuses, forming a yellow syrupy liquid with the aspect of caramel. It fuses at a lower temperature than salicine. Exposed to a great heat, it decomposes, evolving fumes which redden litmus-paper. It leaves no ash. Heated with potash in a tube, its vapours do not restore the colour of reddened litmus. It is very slightly soluble in water, but renders it strongly bitter. The solution is neutral to litmus-paper; it is not precipitated by either neutral or basic acetate of lead, tannin or alkalis. It is soluble in alcohol and æther. Concentrated sulphuric acid dissolves and instantly reddens it; the tint is very deep and tinged with purple. A certain quantity of water causes a precipitate in the solution. The liquid then appears green; as the precipitate subsides, it becomes paler. Ammonia does not dissolve the precipitate, but renders it of an ochreous-yellow colour. Nitric acid dissolves the principle, and the yellow solution thus formed is precipitated by ammonia. Muriatic acid dissolves it, acquiring a tinge of violet, which is converted into blue on the addition of a very small quantity of water. As cascarilline does not contain nitrogen, and combines with neither bases nor acids, it must be ranged among the neutral non-nitrogenous substances, with salicine, columbine, &c. Its intense bitterness, and the general analogy between cascarilla and cinchona, render it probable that it may be advantageously used in medicine.

Chem. Gaz. from Journ. de Pharm. et de Chim.

ART. LXXXV.—NOTE UPON THE PREPARATION OF IRON
REDUCED BY HYDROGEN.

BY MM. E. SOUBEIRAN AND DUBLANG.

IRON reduced by hydrogen, of which the employment was proposed by M. Quevenne, has been adopted in medical practice. It is now prepared in quantity for the use of the hospitals of Paris. It would appear at first sight that nothing could be more simple than to bring about the reduction of the oxide of iron, by a current of hydrogen gas; but when it comes to the trial, considerable difficulty is encountered. It is well known that no one yet has been able to arrive at results as satisfactory as those obtained by our associate Quevenne, who has applied to the study of this operation that patient and enlightened intelligence with which we all know he is endowed. Unfortunately he has not communicated all of his observations, and those have been forced, who have wished to prepare the *reduced iron*, to make a host of attempts, that have not always been successful. M. Thiebierge has published recently an interesting note on this subject; his ingenious apparatus will be useful to those who wish to prepare small quantities of the article, but does not answer the purpose in the more extended manufacture of it.

The reduced iron intended for medicinal use should be presented in the form of a minutely divided powder. The essential condition of success in the operation, consists entirely in the temperature, which, if not sufficiently high, the reduction does not take place; but if too high, the iron is reduced, but becomes agglutinated in ductile laminæ and the operation fails. To heat properly is then the principal object that should be proposed; to multiply the points of contact between the oxide of iron and the hydrogen is a second condition that it is necessary to fulfil; less essential

without doubt, but of importance, if it be desirable not to lose considerable quantities of hydrogen gas.

We have confined ourselves to the employment as a vessel of one of the fountain pipes found in commerce. That which we employed was $4\frac{1}{2}$ inches in diameter, and 22 in length. Such a vessel furnished from 9 to 11 oz. of iron by the operation.

To multiply the surfaces and diminish the proportion of inactive gas, we placed in the tube small floors (diaphragms) of iron gauze, between which were thin bars, the gauze being covered with the oxide; when all were arranged, they presented a solid mass. As the operation proceeded, the powder sank down and the passage of the gas was free.

Besides the pipe of reduction, the apparatus is composed of a large flask for the production of hydrogen gas, of a wide receiver, in which is condensed a part of the water, of a second flask containing concentrated sulphuric acid which dries the gas and serves at the same time as a guide to the operator. By the rapidity of the bubbles which are given off he sees if it be necessary to quicken or retard the disengagement; after leaving this vessel, the hydrogen gas traverses a tube full of chloride of calcium, from which it passes into the iron vessel; escaping from this it is conducted by a glass tube bent at a right angle and inserted beneath the surface of water in the receiver. To adapt the iron vessel easily to the other parts of the apparatus, we employed covers of iron which close it completely, and having in their centres iron tubes about 15 inches long. By means of this arrangement, the apparatus and iron vessel are heated together, and the connexions are sufficiently distant from the fire not to be injured.

We have said that it was necessary that the temperature should be sufficient, and that it should not be too elevated. We obtain a very convenient heat by the following disposition: A small enclosure is made of a range of bricks placed on the ground; upon these bricks is placed an iron grating

and all round the grating a new enclosure of bricks above the lower ones. The height of two bricks gives a proper elevation; it is sufficient that they should be a little higher than the vessel for reduction. A rectangular furnace is thus constructed twenty-two inches long by fifteen broad. The iron pipe traverses the furnace lengthwise; it rests upon a support of bricks upon the grating two inches high. The advantage of this support is the prevention of the lower part of the pipe becoming more heated than the rest. The furnace is filled with charcoal so as to cover the pipe, and a limited escape is permitted to the ashes, so as not to allow the combustion to become too intense. By means of this arrangement the heat is never elevated sufficiently to conglomerate the reduced iron. If the temperature is not sufficiently great, it is perceived by the gas escaping from the extremity of the apparatus in as great abundance as it is formed. It is necessary then to give a little more activity to the fire by increasing the draught.

The oxide which we employ is the safran of Mars, of our Pharmacopœias. I should say however that I have operated with the oxide of iron, which is produced by calcining the oxalate. If this were not more costly, this oxide would merit the preference, for it contains less oxygen than the previous one, and, moreover, possesses less tenuity. It furnishes the most beautiful preparation.

It is necessary to remind those who wish to reduce iron by hydrogen, that it is necessary to wait before heating, until the apparatus has been deprived of air by the first current of gas, and that when the operation has terminated (which is perceived by no more water escaping) it is necessary to withdraw the fire and continue to pass the hydrogen, until the apparatus becomes cold. It is very convenient to adapt to the apparatus two copper stop cocks, one at each end. The current of hydrogen can then be arrested without waiting until the pipe becomes cool, as the cocks can be closed. When cool, the iron is withdrawn and subjected to slight phosphorization.—*Journ. de Pharm.*

EXTRACTS FROM THE MINUTES OF THE PHARMACEUTICAL MEETINGS.

October 6th, 1845.

CHARLES ELLIS, Vice President, in the Chair.

The minutes of the preceding meeting were approved.

There being no written communications, Samuel C. Sheppard called the attention of the meeting to some specimens of blue mass, numbered 1, 2, 3, 4, and 5. The first was manufactured by George W. Ridgeway of this city, the rest of various origin and quality. With a view to their analysis the specimens were referred to Ambrose Smith, Dr. Robert Bridges, and Samuel C. Sheppard, as a committee.

Dillwyn Parrish called the attention of the meeting to a specimen of Bittern, from the salt works of western Pennsylvania, from those springs containing Bromine. This Bittern, or mother water, resulting after the separation of the salt, is a dark coloured liquid, sp. gr. 1.419.

A specimen of bromide of iron was also presented.

Joseph C. Turnpenny remarked that, in mixing hydrarg. cum creta with inspissated ox-gall, the mercury was noticed to separate in considerable quantity without any moisture being added. Another member had observed the same phenomenon when extract of rhubarb was incorporated with the same preparation. The mercurial preparation was of good quality.

William Procter, Jr., exhibited specimens of extract of stramonium, with and without the chlorophylle. The latter was dark colored, and highly efficient.

The same member presented a sample of an article of opium, which had been sold in this city at Comly's auction store, at a third of the market price. It had the aspect of exhausted opium, and was made up into globular and compressed masses. The subject was referred to W. Procter, Jr., J. H. Ecky, and J. C. Turnpenny, for examination.

November 3d, 1845.

Professor BRIDGES in the Chair.

The minutes of the last meeting were read and adopted.

William Procter, Jr., presented to the College, on behalf of Dr. Bridges, its American editor, a copy of Fownes' Manual of Chemistry.

Specimens of the copper ore from Copper Harbor, Lake Superior were also presented.

The committee appointed at the last meeting on the subject of opium, reported :

That they had submitted the opium referred to them to a careful examination, with the view of ascertaining the percentage of morphia it contained. One hundred grains when treated by the process of Dr. Staples, was found to yield three grains of the first crystals. By treating these with ether, the quantity was reduced to 2.65 grains which is about one fourth of the per centage contained in the best Smyrna opium.

An aqueous infusion of this opium gave evidence of the presence of meconic acid by adding a persalt of iron.

All the committee have been able to ascertain in reference to the introduction of the drug is, that it was sent on from Boston and advertised for sale at Comly's auction store, and was there sold, the most of it, with a destination for Baltimore. The cases were small, tin inside, and contained but about forty pounds each. The masses were much of the size and shape of ordinary opium, but quite dry, hard, and possessed of but little of the true opium odor. The masses had no rumex seeds adhering to their surfaces, and altogether possessed the aspect of opium that had been disintegrated by water, and the residue afterwards worked up into masses with the addition of some other matter.

WILLIAM PROCTER, JR.,	} Committee.
JOSEPH TURNPENNY,	
JOHN H. ECKY,	

The report was adopted.

Dr. Bridges on behalf of the committee on Pil. Hydrarg. appointed at the last meeting, reported progress.

December 1st, 1845.

CHARLES ELLIS, Vice President, in the Chair.

The previous minutes were approved.

Silliman's Journal for July and October, were laid on the table.

A sample of Egyptian opium was presented by Thomas P. James, who stated that it was part of the lot that was introduced into this market eight or ten years since. It was found at that time to contain about 7 per cent. of morphia.

A specimen of lactate of soda, was presented by William Procter, Jr.

Dr. Bridges on behalf of the committee on blue pill mass, stated that the committee had been engaged with the duty referred to them, but were not yet prepared to report.

A sample of Gordon's blue mass was referred to the committee for examination.

William Procter, Jr., called the attention of the members to some specimens of acetate of zinc, with a view to the illustration of a new method of purifying that salt from iron. (See page 241 of this volume.)

Charles Ellis stated that an article offered for jalap was in the New York market, which proved to be mechoacan root.

January 5th, 1846.

Professor Carson in the Chair.

The minutes of the last meeting were adopted.

Reports of Committees being in order, Prof. Bridges, on behalf of the Committee on Blue Mass, read their Report.

The committee to whom was referred the examination of the specimens of blue pill mass, which were presented to the college by Samuel C. Sheppard, respectfully present the following report, viz.

Specimen No. 1 had a good pilular consistence and appearance, and was made by George W. Ridgeway of Philadelphia. One hundred grains of this mass was found to contain twenty-eight grs. of mercury.

No. 2 possessed the proper appearance and consistence, maker's name not known. This specimen contained twenty-six per cent. of mercury.

No. 3. This sample to which Clement Cresson's label was attached, was obtained by Samuel C. Sheppard from a stock put up for Dr. Shoemaker of Pennsylvania. Its consistence was so soft as to render it unfit for making pills without the addition of some other substance. One hundred grains yielded twenty-five grains of mercury.

No. 4 was labelled Baily of Wolverhampton, and had a good consistence and color. One hundred grains yielded twenty-five grains of mercury.

No. 5, was labelled "Pil: Hydrarg: L. P." It was dry pulverulent, apparently very old, and contained globules of mercury of sufficient magnitude to be visible to the unassisted eye. It contained thirty-four per cent. of mercury. This specimen probably contains a larger proportion of mercury than when originally prepared, owing to the evaporation of moisture.

These were the samples originally submitted to the committee, but in furtherance of the objects of the report they have examined four other specimens, viz.

No. 6. A second sample of Ridgeway's manufacture obtained from George W. Ridgeway by the committee. Its consistence was good, but the cut surface exhibited several white specks, and by analysis it yielded twenty-eight per cent. of mercury.

This specimen was made with the design of submitting it to the Committee, and the manufacturer states that the full proportion of mercury was employed, that the mill run a few hours longer than usual, and that nothing occurred in the process to which the deficiency could be attributed.

No. 7. A third sample of Ridgeway's manufacture, handed

to the committee soon after No. 6, by G. W. Ridgeway. It possessed an excellent consistence and handsome appearance. One hundred grains yielded by analysis thirty-three grains of mercury.

This specimen was made after No. 6, and with the intention of having it examined by the committee. Its consistence was considered by the maker as more perfect. In making the Blue mass marked No. 7, Mr. Ridgeway states that he employed the ingredients for a fresh portion of the mass and added to it the remainder of No. 6, and worked the whole together.

It is due to Mr. R. to state that the investigation of his article was made at his instance, that he is confident of mixing the ingredients in the full proportion of the pharmacopœia in every instance, and that he cannot account for the deficiency in No. 6.

No. 8. A specimen of blue pill manufactured by Mordecai L. Gordon of Philadelphia, and said to have been made during a leisure period in the summer, and worked up for an unusual length of time. Consistence and appearance good, and contained twenty-six per cent. of mercury.

No. 9. A second sample of M. L. Gordon's make, recently prepared. Appearance good, but softer than No. 8. It yielded thirty-one per cent. of mercury, by analysis.

On further enquiry the committee find that the specimen of Gordon's No. 8, was subjected to the attrition of the mill for two weeks, by steam power, and that the instrument frequently, during that period, acquired a temperature little short of 140° Fahr.—also that the sample No. 9 was treated in the same way for only three days. Now as mercury will volatilize very sensibly at that temperature, and much below it, the committee think that the difference in the proportion of mercury may be owing, in part at least, to this cause, particularly as they have the testimony of the manufacturer that the full proportion of mercury was employed in each case. This is an interesting fact worthy of further investigation, and may throw some light on the cause of

the variable strength of blue pill mass, when within a reasonable approximation to the prescribed quantity. If the experiment of long attrition was repeated, with the precaution of controlling the temperature of the mill, or instrument of manufacture, it would be conclusive as to the volatilization of the mercury being a source of variability.

In conclusion, the committee would observe that the examination of the above specimens, as to the per centage of mercury they contained, was conducted with great care, and they are confident in the accuracy of the results. The method of analysis they found most convenient and at the same time most reliable, is a modification of that of Prof. Reid of the New York College of Pharmacy, described by Mr. Adamson in the XVIIth volume of the American Journal of Pharmacy. The instrument was modified by blowing a bulb on the end of a tube, to contain the blue mass and iron-filings, and then inserting its open extremity, undiminished in diameter and slightly curved, into a vial of alcohol. The heat was applied gradually by means of a spirit lamp, and continued in each experiment for nearly an hour, to insure the perfect separation of the mercury. By suffering the alcohol to rise in the tube by the cooling of the confined air, and again chasing it out by expansion, every particle of mercury was driven into the vial. The empyreumatic oil, etc., was dissolved by the alcohol which was poured off from the mercury, and the latter washed with a second portion of alcohol, and put into a warm place, which evaporating the moisture enables the mercury to coalesce into one globule. In order to be assured of the perfect volatilization of the metal, the contents of one of the bulbs was heated to whiteness without any evidence of mercury. The alcohol, after removal from the mercury, was tested with proto-chloride of tin, without any indication of the former metal, and it is believed that the treatment by boiling with that salt, as recommended by Dr. Reid, is an unnecessary precaution.

As it may be convenient for those who have not paid

particular attention to the examination of blue pill, to have a more explicit statement of the method of ascertaining the proportion of mercury, the following wood cut is annexed :



a A bulb of green glass of the capacity of half a fluid ounce, with the tube bent and inserted through the cork of a one ounce wide mouthed vial; *b* nearly filled with alcohol; *c* the blue pill previously mixed with about one fourth of its weight of iron filings, and rolled into little pellets,

(50 grs. of blue pill mixed with 15 grs. of iron filings is a convenient quantity.) The tube of the bulb should descend a little below the surface of the alcohol, and another tube should pass through the cork to permit the escape of the uncondensed gases. The heat should be gently applied until the vegetable matter is entirely decomposed, and then increased until the bulb is heated to bright redness, which heat should be continued until all the mercury has distilled over.

AMBROSE SMITH,
ROBERT BRIDGES,

On behalf of the Committee.

Philadelphia, January 5th, 1846.

On motion the report was adopted and directed to be published with the minutes.

William Procter, Jr., presented specimens of oleic, margaric, stearic, and sebacic acids, artificial camphor, and valerianate of zinc. He found that three ounces of crystallized artificial camphor (hydrochlorate of camphene,) may be readily obtained by passing slowly the muriatic acid gas yielded by the reaction which takes place when two pounds of sulphuric acid are poured gradually on a pound and a quarter of chloride of sodium, through eight ounces of recently distilled oil of turpentine.

MISCELLANY.

Patent granted to Robert Oxland, Plymouth, Devon, for improvements in the Manufacture of Chlorine.—This invention consists in a method of manufacturing chlorine by the decomposition of hydrochloric acid by atmospheric air. The hydrochloric acid gas and atmospheric air are mixed in the proportion of one measure of the former to two of the latter; and the mixture is passed through an air-tight furnace, kept at a bright red heat. The hydrochloric acid is best obtained by decomposing common salt by sulphuric acid in a furnace or retort so heated that the products of combustion do not mix with the acid gas evolved; and the acid gas should be dried (previous to mixing it with the air) by passing it through a vessel filled with pieces of fire-brick, over which a small stream of sulphuric acid is constantly flowing. The requisite supply of atmospheric air is kept up by pumping it into an iron reservoir, furnished with a stop-cock or valve for regulating the discharge of the air. The decomposing furnace, through which the mixture of hydrochloric acid and air is passed, resembles an ordinary reverberatory furnace in form; but it is so constructed as to admit of the fire passing over the arch and under the bed; by which means the furnace is heated without the fire passing into it. The furnace is filled with pieces of porous pumice-stone, and the gas and air enter at the end furthest from the fire, and pass out at the other end through a pipe at the upper part of the furnace. That part of the furnace nearest the fire should be kept at a bright red heat by a fire acting externally, the smoke passing through flues over the furnace into the chimney.

The products resulting from the admission of hydrochloric acid and atmospheric air into the decomposing furnace consist of chlorine associated with undecomposed muriatic acid, and any excess of atmospheric air and nitrogen. This mixture is cooled by passing it through a series of earthenware tubes surrounded by water; after which the hydrochloric acid is effectually separated by passing the mixture through water; and, finally, the chlorine is obtained, and chloride of lime produced, by passing the residuary mixture into the ordinary lime condenser, where the chlorine is absorbed, and the nitrogen and atmospheric air remaining are allowed to pass into the atmosphere.—*Chem. Gaz.*

Examination of Oil of Amber. By M. DÆPPING.—When we subject amber to dry distillation, it produces empyreumatic oils and resins,

which offer no well determined chemical characters. If we submit these products again to rectification, we obtain a yellow oil, which has been already examined by Elsner, as well as by Messrs. Pelletier and Walter; their labours on this subject have led to nothing decisive. M. Dæpping has not been more fortunate. He confined himself to the task of showing that the rectified oil is plainly of the same composition as essence of turpentine, but that its boiling point is not constant, so that we cannot determine the density of its vapour. Treated with sulphuric acid the oil yields an oily carbonated hydrogen, which also shows a similar composition.—*Chemist, from Journ. de Pharm.*

Formula for Red Ink.—Two ounces of the best Brazil wood, half an ounce of alum, and half an ounce of crystals of tartar are boiled with sixteen ounces of rain or distilled water, down to half its bulk; half an ounce of gum arabic is dissolved in the strained liquid, and finally a tincture made of one and a half drams of cochineal and one and a half ounces of alcohol of 0.839 sp. grav. mixed with it.—*Chem. Gazette.*

The danger of arsenical injections in bodies intended for dissection.—The competition that has recently taken place for the situation of Superintendent of the anatomical labours of the Faculty of Medicine at Montpellier, has shown the danger arising from the employment of arsenic in the preservation of bodies intended for dissection.

Five of the candidates engaged in the dissection of bodies which had been injected with an arsenical solution, were not long before they became a prey to symptoms of a more or less dangerous character. Some were effected in the head with giddiness and dimness of sight, and the intellectual faculties became impaired and painful; others suffered particularly in the gastro-intestinal organs; violent pains, colic, diarrhœa, nausea, and vomitings affected them on the second day of their labour, and were followed by a feverish wakefulness.

In the case of them all one symptom was exhibited which we may call pathognomonic, so much was the characteristic it exhibited uniform and special; all the candidates experienced a most violent shooting and continued pain at the extremity of the fingers. The principal seat of this pain was in the fleshy part of the fingers, and even within the circumference of the nails it seemed impossible for any of the candidates to use an instrument of any description. An examination of the fingers exhibited a swelling at their extremity, and an injection, visible through the substance of the nail, resembling an ecchymosis, and in addition to this a violent pulsation in the collateral arteries; the nail, after a time, completely separated itself from the surrounding tissues wherever the ecchymosis existed.—*Chemist.*

Determination of the Causticity of the Soda Salts of Commerce. By M. BARRISWIL.—Having had occasion to examine, with M. S. Riess, alkalimetrically, some samples of commercial soda, we employed, in order to determine the caustic alkali, a new process of great accuracy, which, although demanding somewhat more time than the ordinary process, is so readily executed that it may be recommended to manufacturers, and in some cases it might certainly be employed with advantage in analytical investigations of the laboratory.

This process is founded on two chemical reactions, both well known, viz:—

1. When an excess of chloride of barium is poured into a solution of carbonate of soda, the filtered liquid is not rendered turbid by carbonic acid.

2. When the least quantity of alkali is added to a perfectly neutral solution of chloride of barium, the filtered liquid is rendered turbid by carbonic acid.

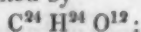
The process of analysis consists in determining the amount of barytes eliminated from the chloride of barium by the caustic alkali contained in the soda salt. For this purpose, 10 grms. of the soda to be assayed are dissolved in water, and to the solution one of 25 grms. of perfectly neutral chloride of barium, that is to say, an excess, added to it. It is now filtered, the filtrate washed, and a current of carbonic acid passed into the filtered liquid, which is then heated to boiling; the precipitate collected, washed and weighed. 1 equiv. of carbonate of barytes corresponds to 1 equiv. of caustic soda. This process, which we have frequently employed, has enabled us to detect less than 1 per cent. of caustic alkali in a soda salt, and to convince ourselves that certain samples, which were said to contain from 1 to 2 per cent. of free alkali, contained not the least trace. These samples were very rich sodas of remarkable purity; submitted to the alkalimetric test by Gay-Lussac's method, they saturated $58\frac{1}{2}$ measures of the test-liquor, according to which they should contain 99 per cent. of pure and dry carbonate of soda. Astonished to meet in a commercial product, made on so large a scale, so remarkable a purity, we verified with chemically pure carbonate of soda our alkalimetric liquid, which had however been made with the greatest care. It required exactly $59\frac{1}{2}$ divisions of the tube for 3.185 grms. of the soda salt. With nitrate of silver and chloride of barium, we obtained scarcely perceptible precipitates in the solution of soda previously saturated with nitric acid. One single crystallization removed the last traces of impurity.—*Chem. Gaz. from Jour. de Pharm.*

New and economical process for preparing oxide of Carbon.—By M. FILHOL.—In the memoir which he published a short time ago on lactic acid, M. Pelcuze noticed the following reaction as being very curious.

When we make a mixture of lactic acid and concentrated sulphuric acid, the latter acid being in great excess, we obtain, by gently heating the vessel which contains it, an abundant disengagement of pure oxide of carbon.

In reflecting on the relation of composition which exists between sugar and lactic acid, I was led to think that it was not impossible that a similar action might be established if sugar was substituted for lactic acid in the foregoing mixture.

The formula of crystallized cane sugar is $C^{24} H^{22} O^{11}$; that of hydrated lactic acid is represented by



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thus, therefore, if the elements of 1 equivalent of water be subtracted from the elements of 2 equivalents of lactic acid, we have the formula of crystallised cane sugar.

If we admit, with M. Juérin Vary, that the formula of anhydrous sugar of starch is $C^{24} H^{24} O^{12}$, it is evident that 2 atoms of lactic acid would just contain the elements of 1 atom of anhydrous sugar of fecula.

I heated in a matrass 20 grammes of cane sugar with 80 grammes of concentrated sulphuric acid; the mixture being maintained at a very gentle heat, a very brisk reaction was manifested, a very abundant disengagement of gas was produced, the mass swelled up, turned black, and became almost solid; I then stopped the operation. I had collected about 2 quarts of gas.

This gas formed, as was proved by the analysis which I made, of a mixture of carbonic acid and oxide of carbon. I ascertained that it contained about one-fifth of its volume of carbonic acid. I should say, moreover, that the composition of the mixture varies in each operation.

Deprived, by washing with lime water, of all its carbolic acid, this gas is colorless; it does not redden litmus; it is decomposed at a red heat of potassium, which absorbs its oxygen and produces a positive carbon; it burns with a pure blue flame. I proved by eudiometrical analysis that it consisted solely of carbon. Sugar of starch and fecula furnished analogous results, as it is evident, the reaction of sulphuric acid on sugar or starch differs from that which the same acid exerts on lactic acid, inasmuch as, with the latter acid, the oxide of carbon is obtained without the mixture of carbonic acid, but the separation of the latter is so easy that it will always be more economical to employ sugar.

This process, which is much more economical than all those which have ordinarily been used, is so easy of execution, that I have reason to hope that it will be adopted in all laboratories for the preparation of oxide of carbon.—*Chem. from Journ. de Pharm.*

To ascertain the purity of Myrrh. By M. RICHINI.—Let it be finely pulverised and saturated for a quarter of an hour, with an equal weight of sal-ammoniac in powder, then add gradually fifteen times its weight of water. If the mixed powder dissolves quickly and entirely, the myrrh is pure.—*Chem. from Journ. de Chem. Med.*

Formula for Bochet's Ioduretted Syrup.—The formula of this syrup, which is very much in use at Lyons, has been communicated to us by M. Bertrand, pharmacien of that city. It is the following:—

R. Sarsaparilla	-	} aa 1 kil.
Sassafras	-	
Guaiacum	-	
Squills	-	
Senna	-	

Two decoctions are made in a sufficient quantity of water; they are mixed and reduced to 8 kilogr.; 5 kil. of sugar and 5 kil. of honey are added; it is clarified with white of egg, and a syrup is made at 28°; it is heated after cooling, and 125 grammes of the tincture of iodine of the codex is added.

This syrup contains per 100 grammes, 1 gramme of the tincture. It is advantageously employed in swellings of the glands, especially of the thyroid gland, rachitis, scrofulous affections, degenerated venereal diseases and gout. A great number of cures have proved its efficacy.—*Ib. from Chem. Gaz.*

On a new Product resulting from the Decomposition of Urea. By FR. WÖHLER, and J. LIEBIG.—When perfectly pure dry urea is submitted to slow distillation, the greater portion of it is converted, not into cyanuric acid, but into a new body, which may be regarded as cyanurate of ammonia from which the elements of 2 equiv. carbonic acid have separated. In its behaviour it belongs to the series of the melon compounds. On exhausting the residue of the distillation with a large quantity of boiling water, this product of the decomposition remains undissolved. In its dry state it forms a shining white powder, and is perfectly insoluble in boiling water, readily soluble in alkalis and acids, from which it is precipitated on neutralization. On the further action of these solvents, it is decomposed into ammonia and cyanic acid. Heated when dry, it leaves a lemon coloured residue, which on strong ignition is decomposed into cyanogen gas and nitrogen. The formula for this compound is $C^6N^4H^4O^4$.—*Chem. Gaz. from Ann. der Chem. und Pharm.*

On the Chemical Constituents of the Flores Chamomilla Romana and anthemis nobilis.—M. Schendler has separated a peculiar acid from the

Roman chamomile, which greatly resembles valerianic acid, if it be not identical with it. He however only obtained $2\frac{1}{2}$ drms. from 24 lbs. of dry flowers, while the same quantity yielded from 4 to 6 ozs. of the most beautiful essential oil, therefore far more than is usually stated. From flowers which had been kept for a long time much less essential oil is obtained than from fresh. The author, on distilling the flowers of *Anthemis nobilis*, obtained 1.17-1.10 per cent oil and 0.81 per cent. of a peculiar volatile acid, while Wyss obtained only traces of it in his analysis.—*Ibid*, from *Archiv. der Pharm.*

On the Artificial Production of Diaphanous Quartz. By M. EBELMEN.—When either of the two silicic æthers which I have recently described is exposed to the continued action of a moist atmosphere, the liquid finally solidifies to a transparent mass. This product, very delicate and fragile in the first days after its solidification, contracts more and more under the influence of the moist air still remaining diaphanous. Two or three months are requisite in operating on 5 or 6 grms. of æther, for the substance to cease to lose in weight and for its molecular movement to terminate. The substance prepared as above is hard, faintly scratches glass, and possesses great cohesion; its lustre, its fracture and transparency are perfectly comparable to the most beautiful rock crystal. Its density is 1.77. It is a hydrate, which contains twice as much oxygen in the silica as in the water, the formula of which is consequently $(\text{SiO})^2 \text{HO}$.

It is essential, in order that the product may not become fissured during the contraction it experiences before attaining the definite formula $(\text{SiO})^2 \text{HO}$, not to allow the moist air to enter except by an aperture of very small diameter. During the whole of the experiment the flask containing the silicic æther exhales an alcoholic odour, which persists a long time after the solidification, proving that only a portion of the organic matter had separated from the silica when the solidification took place. The contraction proceeds the more slowly the less easily the moist air is renewed in the apparatus, and this slowness appears indispensable to the success of the operation.

From the properties of the hydrate of silica, we may be allowed to hope that it may be turned to advantage in the construction of optical instruments. It is my intention to make some experiments in this direction.—*Ibid*, from *Comp. Rendus*.

On the Artificial Production of Hydrophane. By M. EBELMEN.—By slightly modifying the process for the preparation of hydrate of silica,

described in the preceding paper, there is obtained, instead of a diaphanous product, an opaque substance, which becomes entirely transparent when placed in water, in a word, true hydrophane. It suffices for this purpose that the silicic æther employed retain a little chloride of silicium, which happens when an excess of alcohol has not been employed in the preparation of the æther. On exposing this æther, still somewhat acid, to the action of moist air, there is obtained a solid mass, which is at first transparent, but ends by becoming opaque after some week's exposure to the air. The translucidity of this substance is so much the less the greater the proportion of the chloride of silicium in the æther. Some of the fragments have the semi-transparency of opal. They all become entirely transparent in water.

We are therefore able artificially to reproduce hydrophane, this rare variety of quartz, and the curious property of which had struck mineralogists.

A very small proportion of foreign substances suffices in fact to modify the translucidity and the appearance of the hydrate of silica; thus a small flask containing silicic æther having been closed by mistake with a cork, which belonged to a bottle full of creosote, the æther, on becoming coagulated under the action of moist air, yielded a slightly yellowish silica, and merely translucent like chalcedony; the product thus obtained was not hydrophanous.

I propose to continue and to vary these experiments, which appear to me of great importance and of considerable interest.—*Ibid*, from *Comp. Rendus*.

Indelible Ink—May be prepared by adding lamp-black and indigo to a solution of the gluten of wheat in acetic acid. This ink is of a beautiful black colour, at the same time cheap, and cannot be removed by water, chlorine, or dilute acids. M. Herberger gives the following directions for its preparation:—Wheat-gluten is carefully freed from the starch, and then dissolved in a little weak acetic acid; the liquid is now mixed with so much rain-water that the solution has about the strength of wine-vinegar, i. e. neutralizes one-sixteenth of its weight of carbonate of soda. 10 grs. of the best lamp-black and 2 grs. of indigo are mixed with 4 oz. of the solution of gluten and a little oil of cloves added. This ink cannot be employed for marking linen, as it does not resist mechanical force.—*Ibid*, from *Jahrb. für Prakt. Pharm.*

Detection of Impurities in Disulphate of Quinine.—The following test for the adulteration of disulphate of quinine is recommended by Dr. Nevius of Liverpool, on account of its delicacy and simplicity:—To 1 or 2 grs. of the suspected salt add 3 or 4 drops of sulphuric acid in a white

evaporating dish, and twice as many drops of water. If the salt contains either fatty matter or starch, these will remain; whilst, if they are absent, the whole will be dissolved. Next apply heat to the solution, and as it becomes concentrated the acid will char any sugar which may be present, which will be indicated by a black stain round the edge of the solution, and the whole will speedily assume the same colour. By this means 1 or 2 per cent. of organic matter may be recognised in as many minutes without trouble. It is said that salicine is an occasional adulteration, and, if present, it is detected by the same proceeding. If a very minute quantity only is mixed with the quinine, blood-red points, and ultimately a general reddish colour, are produced as the concentration proceeds. It is a good plan to observe the effect of the sulphuric acid before the addition of water, as it acts upon the salicine cold, producing the blood-red colour. Thus the single test of sulphuric acid, diluted and heated, detects nearly every impurity which is found in the disulphate; for starch fatty matters and insoluble earthy salts are left undissolved before the application of heat, and salicine, gum and sugar are shown by the effects of heat on the solution. Pure disulphate of quinine is not affected by sulphuric acid applied as above.—*Ibid*, from *Lancet*.

NOTE.—In the article on a new caustic by M. Velpeau, page 277 of this number, which has been extracted from the *London Chemist*, it is stated that the *Safran of Mars* is employed to fix sulphuric acid. It should have been stated *saffron*, which is carbonized and undergoes a CHANGE in accordance with the statement in the paper.—EDITOR.

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